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ULTRAFAST CARRIER AND LATTICE DYNAMICS IN SEMICONDUCTORS

by

Michael David Cummings



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirement for the degree of Master of Science

Department of Electrical and Computer Engineering

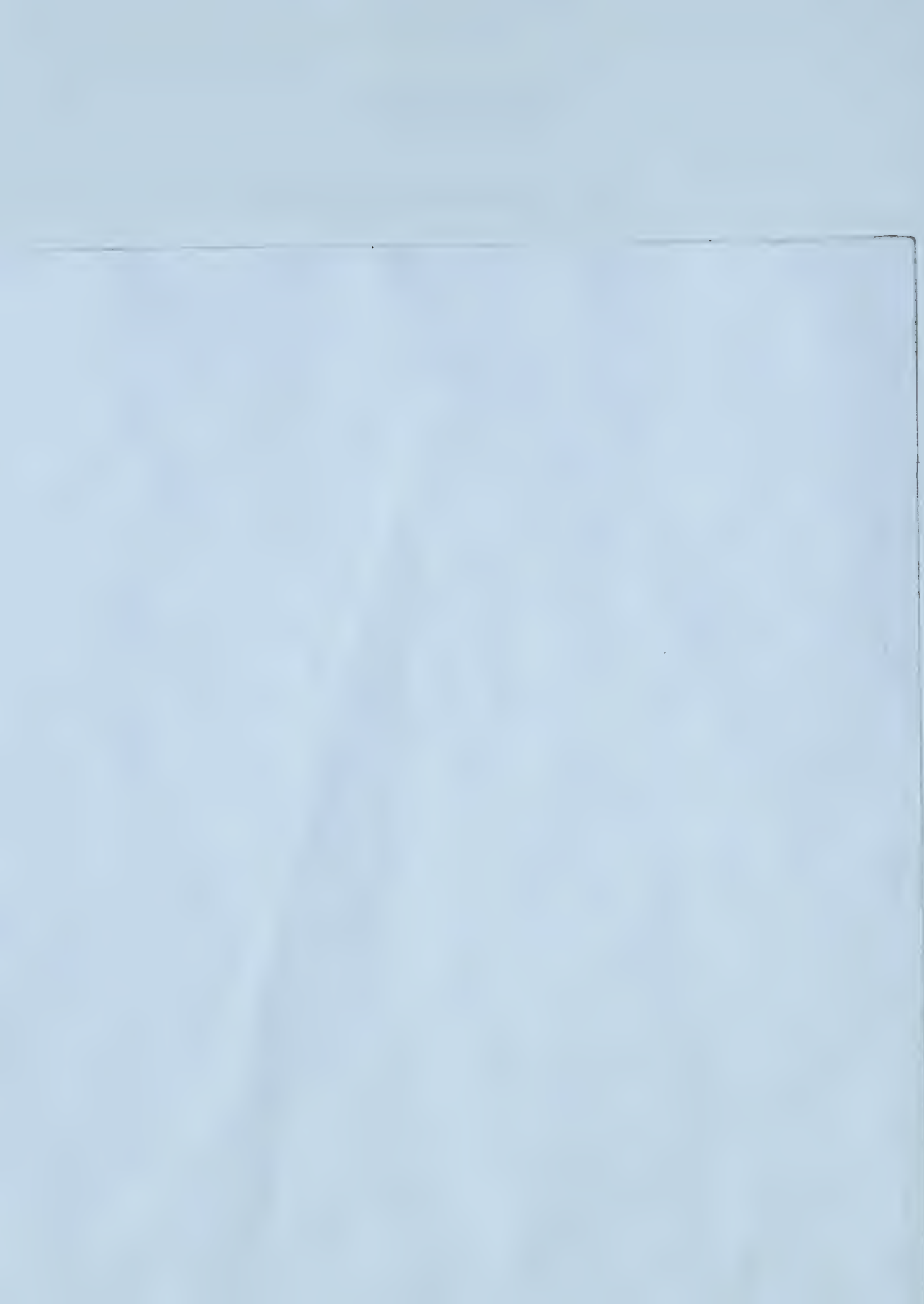
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The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled ULTRAFAST CARRIER AND LATTICE DYNAMICS IN SEMICONDUCTORS submitted by Michael David Cummings in partial fulfillment of the requirement for the degree of Master of Science.



Abstract

Utilising a transient pump-probe reflectivity experimental system, the lattice and carrier dynamics of GaAs and InSb are explored on sub-picosecond timescales. In GaAs, the sub-200 fs behaviour of photo-excited charge carriers is observed and a model is constructed, based on the third order polarization response, to extract the time constants of carrier relaxation.

Measurements of an edge-illuminated GaAs photo-conductive (PC) switch demonstrate that carriers screen the local field within 100 fs of photo-excitation and participate in the generation of an ultrashort electrical transient. Plasmon-phonon modes produced at the longitudinal-optic (LO) and transverse-optic (TO) phonon frequencies indicate the lattice participates in the field screening process.

The first time domain observation of coherent longitudinal acoustic (LA) phonons resulting from a very high photo-generated carrier density in InSb is presented. A frequency shift of one phonon mode indicates the lattice is approaching an unstable regime for laser fluences significantly below the damage threshold.

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List of Acronyms

APB	Angular pulse broadening
ASF	Anisotropic state filling
BG	Band gap
CB	Conduction band
c-c	Carrier-carrier
c-ph	Carrier-phonon
DECP	Displacive excitation of coherent phonons
e-e	Electron-electron
e-h	Electron-hole
FWHM	Full width at half maximum
GaAs	Gallium Arsenide
GVD	Group velocity dispersion
hh	Heavy-hole
h-h	Hole-hole
IMP	Instantaneous Macroscopic Polarization
InSb	Indium Antimonide
LA	Longitudinal acoustic
lh	Light-hole
LO	Longitudinal optic
PC	Photo-conductive
SO	Split-off band
SI	Semi-insulating

TA	Transverse acoustic
TO	Transverse optic
VB	Valence band

Chapter 1

Introduction

The advent within the past decade of commercially available pulsed laser systems capable of producing optical pulses of less than 20 fs in duration has lead to dramatic advances in our knowledge of short timescale semiconductor physics. This understanding is more crucial now than ever before, as device bandwidths begin to push beyond 100 GHz, as the material dynamics occurring on picosecond timescales will influence the workings of such devices. In particular, the advance of terahertz (THz) technologies implies the carrier and lattice dynamics in the semiconductors utilised for these devices be determined on femtosecond timescales.

One of the most versatile techniques for the induction and subsequent observation of the temporal photo-excited charge carrier dynamics within a semiconductor is time-resolved pump-probe reflectivity measurement. Through the use of an ultrashort pulsed laser to both excite the material and probe the resultant changes, a variety of processes in semiconductors, such as the initial carrier-carrier collision or coherent carrier-lattice oscillations, can be observed in great detail and with a high degree of reproducibility. Thus, through this experimental technique the validity of the current fundamental theories of femtosecond semiconductor physics may be readily tested.

1.1 Thesis Objectives

The aim of this thesis is to present three separate applications of time-resolved pump-probe reflectivity experimental techniques conducted on sub-picosecond timescales in the study of carrier and lattice dynamics in III-V semiconductors. The time-resolved data from the experimental investigation of sub-picosecond carrier dynamics in GaAs is analysed via application of an empirical fitting routine to extract the initial carrier relaxation time constants. A PC switch serves as the next system of study, where the influence of the carrier-lattice oscillations on the field characteristics within the switch is presented. In addition, the generation of an extremely high charge carrier density in InSb is shown to generate longitudinal acoustic (LA)-phonons and lead to the softening of these lattice modes.

1.2 Thesis Organisation

Contained in this thesis are seven chapters and one appendix detailing both the experimental and theoretical work performed.

In Chapter 2, the background knowledge necessary for the interpretation of time-resolved pump-probe reflectivity measurements is explained. This includes information on the basic experimental set-up and information on the effects which act to restrict the temporal resolution of a measurement. Some background information on the semiconductor physics relevant to the sub-picosecond timescales is outlined and a brief introduction to the mathematical nature in which the pump-probe-induced material changes are echoed in the reflectivity signal is given.

The primary focus of Chapter 3 is to introduce phonon and plasmon dynamics that may be induced by the generation of charge carriers in a semiconductor. A brief background on phonon physics is followed by a discussion of coupling between phonon and plasmon modes. Then, the concept of mode softening is discussed, in the context of how it relates to the stability of the crystal structure. A final section explains the manner in which the plasmon or phonon oscillations influence the reflectivity coefficient of a material.

In Chapter 4, an experimental measurement of the transient reflectivity signal in GaAs and theoretical model to fit the resultant data is described. First, the time-resolved pump-probe reflectivity experimental set-up utilised in all subsequent chapters is outlined. This set-up is applied to the observation of the transient reflectivity in GaAs due to the dynamics of a moderately large density of photo-generated charge carriers on sub-picosecond timescales. An empirical model is developed in order to extract fundamental time constants relating to the ultrafast momentum dephasing and energy relaxation of the charge carriers.

The ultrashort timescale dynamics which occur in a voltage biased PC switch is the topic of discussion in Chapter 5. The chapter opens with a brief introduction to the central concepts which are relevant in the sub-picosecond study of PC switches. This is followed by a discussion of the results of the time-resolved reflectivity study on the dynamics within an edge-illuminated PC switch. Field screening is shown to result from both the charge carrier ballistic acceleration and plasmon-phonon coupled modes.

In Chapter 6, a time-resolved reflectivity experiment on the effect of the photo-generation of a very high density of charge carriers in InSb is examined. The generation

of coherent LA-phonon modes is observed above a threshold pump energy fluence. From the frequency characteristics of the observed phonon modes it is apparent that ‘mode softening’ is occurring, demonstrating that the InSb lattice is moving towards an unstable regime at energy fluences significantly below the damage threshold.

Finally, a summary of the work presented in each section of the thesis is given in Chapter 7.

Chapter 2

Background Information on Ultrafast Semiconductor Optics

2.0 Introduction

The purpose of this chapter is to outline the important physical and experimental concepts relevant to the present study of the femtosecond electrical and thermal properties of semiconductors by optical means. The chapter will open with an introduction to the experimental technique utilised in the current work, known as time-resolved pump-probe reflectivity. This is followed by a review of the semiconductor femtosecond timescale physics that plays a crucial role in shaping the signals measured in ultrafast pump-probe experiments. A mathematical treatment of reflectivity measurement is the next topic of discussion. In particular, the form in which the optical parameters of a material appear in the measured reflectivity signal and the importance of the pump and probe laser polarizations will become apparent. The chapter will conclude with an examination of the mechanisms which act to temporally broaden the optical pump and probe pulses and how best to limit these effects on the temporal resolution of the experiment.

2.1 Time-Resolved Pump-Probe Reflectivity Measurement

Over the last decade robust commercial laser systems capable of producing sub-100 fs laser pulses over a wide range of wavelengths and powers have become available. As a result the high temporal resolution study of optically induced ultrafast processes in

semiconductors has become a prominent field of research. Following irradiation by an ultrashort laser pulse the underlying physical mechanisms which govern the sub-picosecond behaviour of the semiconductor can often be clearly seen in the time evolution of the material absorption coefficient. As the absorption coefficient is related to both the transmitted and reflected intensity coefficients sub-picosecond material dynamics are often measured via time-resolved pump-probe transmission, absorption or reflectivity experiments [1-6]. Of the three techniques, time-resolved experiments which measure the time evolution of the reflected intensity require the least amount of sample preparation. In order to observe a signal in a transmission or absorption experiment the measurement beam must travel through the sample of interest. Due to the relatively short absorption depth, δ , at optical wavelengths in most semiconductor materials ($\delta < 1 \mu\text{m}$) thin samples must be either created through highly specialized techniques, such as growth by molecular beam epitaxy (MBE), or bulk samples must be reduced to sub-micron thickness. Contrary to absorption or transmission measurements, the only constraint on the material thickness for reflectivity studies is that it must be greater than a few tens of atomic layers- mass produced wafers satisfy this criteria. Thus, in terms of simplicity and minimum financial impact, transient reflectivity investigations are the logical choice.

The basic design for a time-resolved pump-probe reflectivity experimental set-up can be seen in Figure 2.1.1. A clear understanding can be most readily achieved by following the path of a single optical pulse from a laser source. Initially, the output optical pulse is passed through a beam splitter which divides the output intensity into an intense pump pulse and a several times less intense probe pulse. This difference in intensity between the pump and probe pulses is imperative in many experiments to prevent the act of

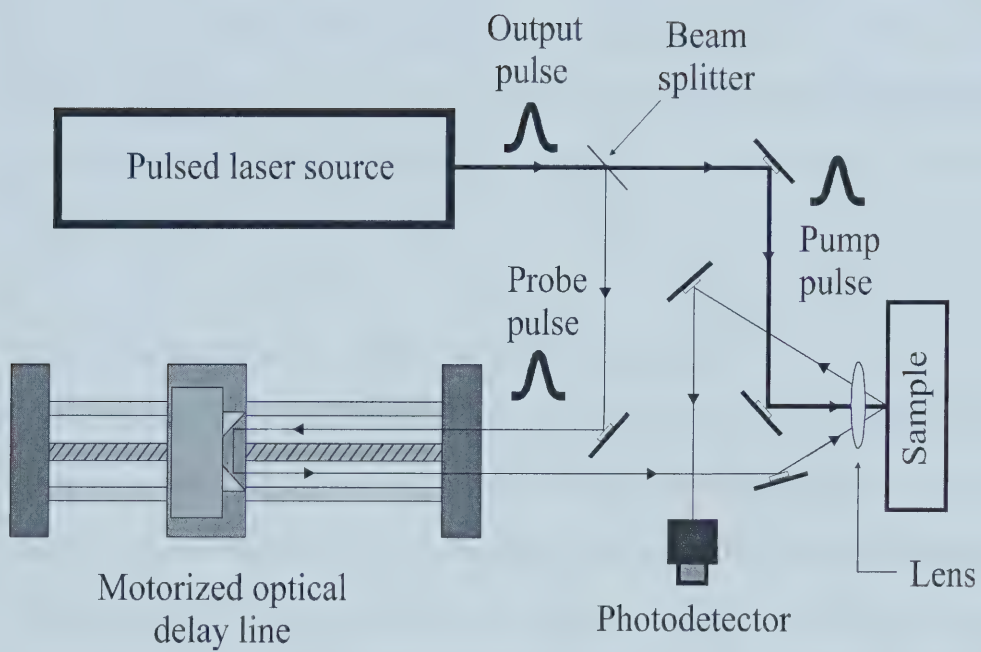


Figure 2.1.1. A simplified transient pump-probe reflectivity experimental set-up.

probing from altering the material, hence, affecting the measurement. Both pulses are directed towards the sample but, due to a shorter optical path length, the pump beam strikes the sample first, thereby inducing a change in the optical properties of the material which will evolve in time as the material attempts to return to the initial equilibrium state. A short while later the probe pulse is directed onto the sample, typically at the location of the pump spot, and its reflected intensity, R , is measured by a photodetector. This procedure is repeated for varying delay times, τ , between the arrival of the pump and probe pulses, thus, a plot of the reflected intensity as a function of time, $R(\tau)$, can be made.

2.2 Ultrafast Processes in Photo-excited Semiconductors

The instant a laser pulse interacts with a semiconductor a vast number of complex processes are set into motion. For photon energies exceeding the material band gap energy, the generation of charge carriers may result in several different populations of electrons and holes with a range of excess energies, momenta and effective masses. Interaction between these carriers causes a redistribution of their momentum and energy distributions while carrier-lattice interaction causes the total energy of the carrier system to be reduced. Spatial redistribution, due to concentration gradients, surface or photo-induced fields and electron-hole recombination may also occur. As well, the introduction of carriers on ultrashort timescales may result in coherent characteristics, such as third order electric field processes or the induction of coherent lattice oscillations. The response of a semiconductor to laser illumination is highly dependent on certain material characteristics. These characteristics vary strongly with the crystal structure, purity and

elemental composition, not to mention the laser intensity, photon energy and pulse duration.

This section begins with some background information on semiconductor energy band theory, a crucial element determining the semiconductor response to illumination. Next, the photo-generated carrier populations and their relation to the incident laser pulse are elucidated upon. The section concludes with a discussion of the carrier-carrier (c-c) and carrier-phonon (c-ph) interactions which drive the evolution of the carrier momentum and energy distribution functions.

2.2.1 Energy Band Structure

The special properties of semiconductors, such as their conductive behaviour upon illumination by laser light above some threshold photon energy, are directly related to the spatial periodicity of the atoms which make up the crystal. This orderly arrangement of atoms places limitations on the energy and momentum states available to a charge carrier which, in turn, affects the optical properties of the material. Naturally, the exact behaviour under illumination varies from material to material but certain classes of semiconductors exhibit very similar responses. The following discussion will be primarily limited to III-V semiconductors. In terms of structure, all III-V semiconductors are zincblende crystals, which means they belong to the cubic symmetry class $\bar{4}3m$. Besides the restrictions this symmetry places on the optical susceptibilities of the material, it also plays a central role in the shape of the energy band structure.

Pictured in Figure 2.2.1a is a simplified energy band diagram, representative of a III-V semiconductor, which must be followed by any free or bound charge carrier within the

crystal. Here, $\mathbf{k}$ is the wave vector of a charge carrier, and is directly related to the carrier's momentum, $\mathbf{p}$, through:

$$\mathbf{p} = \hbar\mathbf{k}, \quad (2.2.1)$$

where: $\hbar = 1.055 \times 10^{-34}$ J·s is Planck's constant divided by 2π . Of particular interest in most laser-semiconductor interactions at optical wavelengths are the lowest conduction band (CB) and the three highest valence bands (VBs). In the CB, three energetic minima are observed, with a global minimum occurring at the Γ -point ($\mathbf{k} = [0,0,0]$) and two subsidiary minima at the L- and X-points ($\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ and $[1,0,0]$, respectively). For an electron confined to one of the energy valleys in the regions near the Γ -, L- and, X-points, characteristics such as mobility or mass will depend greatly on which valley the electron has been confined to. Directly underneath the Γ -minimum are three VB maxima, the heavy-hole (hh), light-hole (lh) and split off (SO) bands, with the hh- and lh-bands being degenerate at the Γ -point. Electrons occupying these three bands are in a bound state and are not able to freely move throughout the crystal.

Typical laser-semiconductor interactions involve laser photons of energies above the band gap energy, E_g , promoting an electron from one of the three highest valence bands (VB) to the conduction band (CB) and simultaneously creating the electron's conjugate particle, the hole, in the same VB from which the electron originated. In such an interaction energy and momentum must be conserved. As the conduction band global minimum and valence band maximum occur at the same $\mathbf{k}$ -value (see Figure 2.2.1a), III-V semiconductors belong to the direct band gap semiconductor class. That is, photo-excitation of an electron from the VB to the CB conserves both momentum and energy without any additional momentum transfer. In an indirect band gap semiconductor, such

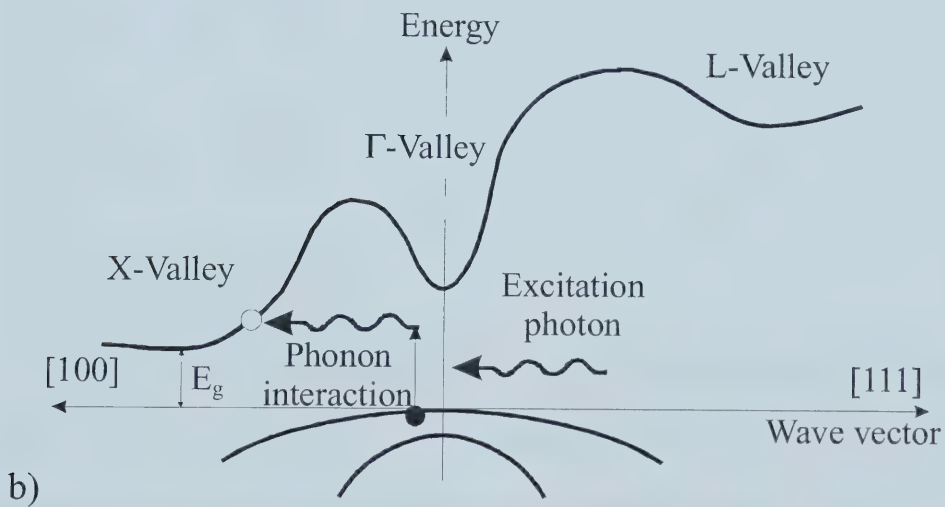
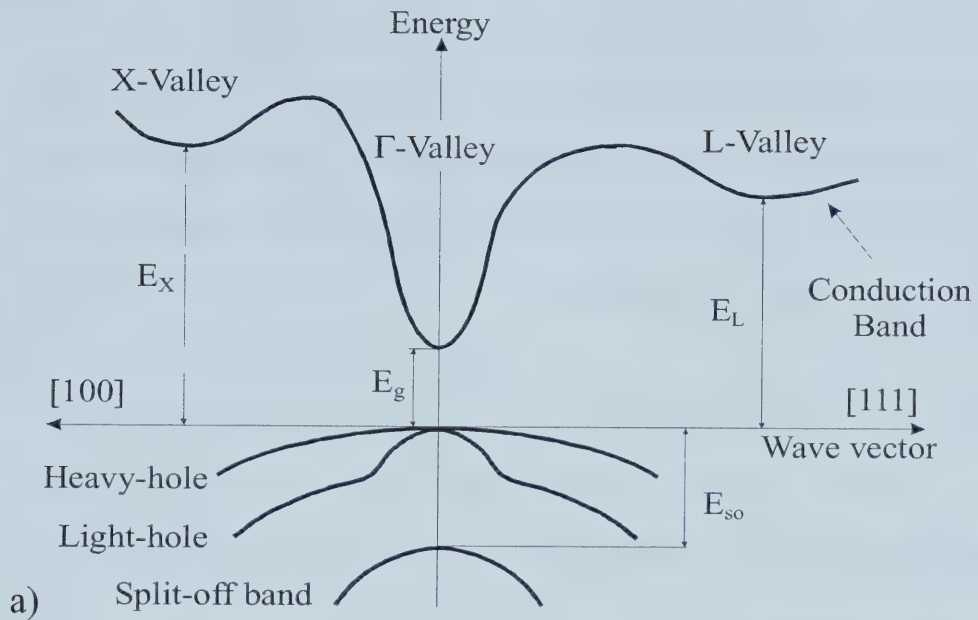


Figure 2.2.1. Simplified band structure diagrams for: a) a direct band gap semiconductor. b) an indirect band gap semiconductor showing the inclusion of a phonon in the absorption process.

as silicon, the global CB minimum and VB maximum are displaced in $\mathbf{k}$ -space, as can be seen in Figure 2.2.1b. Thus, momentum conservation requires the involvement of another particle in the interaction, such as a phonon, for carrier excitation to occur. This important distinction between direct and indirect band gap semiconductors is responsible for drastically different properties, as seen in calculations of the absorption coefficient [7] or ballistic carrier transport experiments [8].

Once electrons are excited to the CB and holes created in the VB, these charge carriers will have a characteristic kinetic energy and momentum. The charge carrier energy in a region about the Γ -point can be described, under the parabolic approximation, as:

$$E_{CB} = E_g + \frac{\hbar^2 |\mathbf{k}|^2}{2m_e^*}, \quad (2.2.2a)$$

$$E_{VB_{hh, lh}} = -\frac{\hbar^2 |\mathbf{k}|^2}{2m_{hh, lh}^*}, \quad (2.2.2b)$$

$$E_{SO} = -\Delta E_{SO} - \frac{\hbar^2 |\mathbf{k}|^2}{2m_{SO}^*}, \quad (2.2.2c)$$

where: ΔE_{SO} is the energy difference between the SO-VB and the hh/lh-VB maximum at the Γ -point, and m_e^* , m_{hh}^* , m_{lh}^* , m_{SO}^* are the effective masses of an electron, hh-, lh- and SO-hole. The above mentioned effective mass encodes information on the crystal-charge carrier interaction and is generally different from the bare electron mass, m_e . It can be shown [9] that the effective mass of a charge carrier is proportional to the radius of curvature of the energy band in $\mathbf{k}$ -space. Hence, bands with a large radius of curvature have a greater effective mass than those with a small radius of curvature.

2.2.2 Charge Carrier Densities

In the limit of small incident laser intensities it is often assumed that the excitation of a semiconductor with above band gap photon energy leads to the generation of charge carriers, with a one-to-one correspondence between the number of photons and number of carriers in the CB. This assertion allows for a simple calculation of the number density of charge carriers, N , generated by a single laser pulse, assuming no other number density processes are involved:

$$N = \frac{I(1-R)}{T_{rep} \delta h\nu}, \quad (2.2.3)$$

where: I is the incident laser intensity, R is the reflected intensity coefficient, T_{rep} is the repetition rate of the laser, and $h\nu$ incident photon energy. In actuality, there are several considerations that affect the number density of charge carriers that may be generated:

1) *Density of states*

Quantum mechanics places certain restrictions on the number of carriers that can occupy any energy region in **k**-space within a given energy band. It can be shown that the density of allowed states in a certain energy range and in the approximation of a single, parabolic band is given by [9]:

$$N_s = \frac{(2m^* \Delta E)^{\frac{3}{2}}}{3\pi^2 \hbar^3}, \quad (2.2.4)$$

where: ΔE is the energy range of interest. The density of states over the entire CB will typically be on the order of the number density of atoms in the material in question (for III-V semiconductors, $N_s \sim 10^{22} - 10^{23} \text{ cm}^{-3}$), while within a specific energy interval (i.e. energy distribution width of a pulsed laser) the density of allowed states will normally be several orders of magnitude smaller. A consequence of the limited

density of states is that if all the states in either the CB or VB are filled then charge carrier excitation cannot occur and, therefore, the material may become transparent to the incident photons.

2) *Higher energy bands*

The conduction band structure is often made up of several distinct bands, thus, excitation to higher conduction bands is permissible if the energy and momentum conservation laws are met. This is especially important if higher order excitation processes, such as multi-photon absorption, occur. In the case of two-photon absorption, populations of charge carriers may develop in two separate conduction bands, one due to single photon absorption and one due to two photon absorption, as illustrated in Figure 2.2.2. Thus, the density of available states will be higher than for pure single-photon absorption. In this case the number density, N , can be calculated as:

$$N = \alpha \left[\frac{I(1-R)}{T_{rep}} \right] \left(\frac{1}{h\nu} \right) + \tilde{\beta} \left[\frac{I(1-R)}{T_{rep}} \right]^2 \left(\frac{1}{2h\nu} \right) \frac{1}{\tau_p}, \quad (2.2.5)$$

where: α is the single-photon absorption coefficient ($\alpha = 1/\delta$), $\tilde{\beta}$ is the 2-photon absorption coefficient, and τ_p is the incident laser temporal pulse width. The nonlinear nature of this interaction is clearly seen through the dependence of the number density on the square of the incident laser intensity.

3) *Number density altering processes*

If the charge carrier generation process is not assumed to be nearly instantaneous the local charge density can be affected by other processes which may occur in semiconductor. In particular, large surface or applied fields of several tens of kV/cm

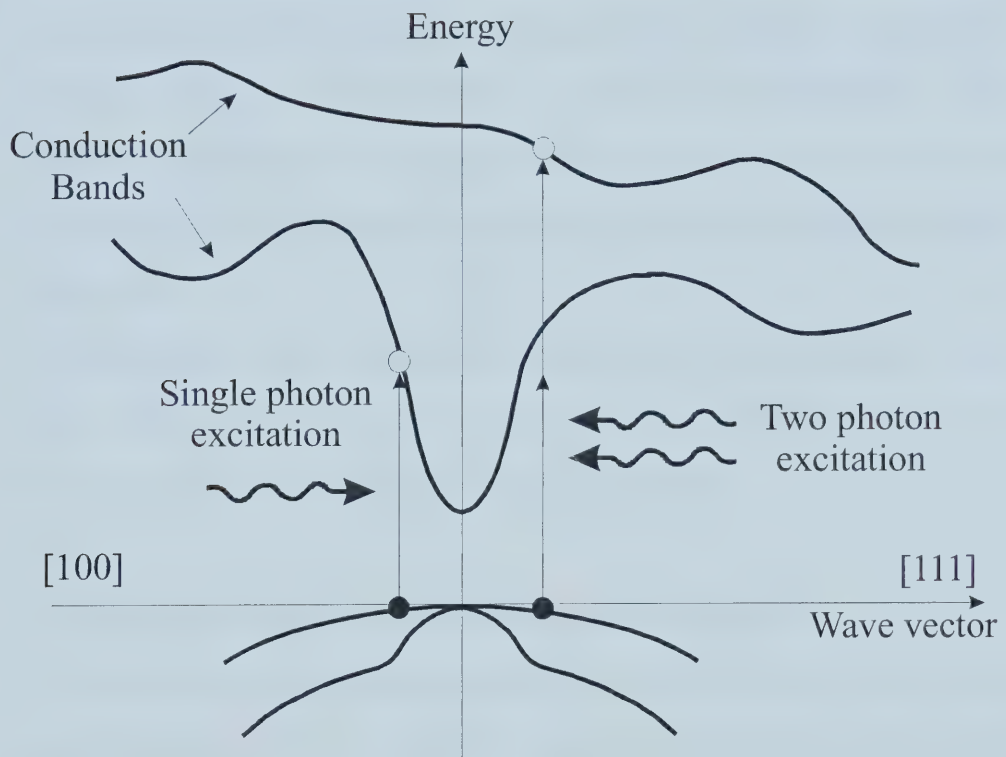


Figure 2.2.2. Band diagram representation of 1- and 2-photon absorption in the case where more than one conduction band is energetically accessible.

can quickly sweep charge carriers out of the excitation region. Equally as important, the charge carrier density can be enhanced as carriers attain enough excess energy to liberate more carriers via impact ionization. Another factor is carrier diffusion, especially in high mobility semiconductors. In materials such as $\text{InAs}_{1-x}\text{Sb}_x$, diffusion can cause photo-generated charge carriers to diffuse on the order of the absorption depth within 100-200 fs. As well, in short carrier lifetime materials, such as radiation damaged silicon or low-temperature (LT-) GaAs, the recombination time for electrons and holes can be as short as a few hundred femtoseconds [10]. Thus, carrier generation and recombination may occur nearly simultaneously even for ultrashort laser pulses.

As most processes in semiconductors depend strongly on the local charge carrier density, accurate interpretation of the material dynamics requires a thorough knowledge of the relative importance of each of the above mentioned processes.

2.2.3 Factors Affecting the Charge Carrier Energy Distribution

While the carrier density plays an important role in the dynamics in semiconductors another vital factor is the distribution of energy and momentum amongst the photo-excited charge carriers. Excitation of a semiconductor with above band gap laser radiation can create several separate populations of charge carriers in the conduction and valence bands of the semiconductor. The probability of finding an electron or hole in a certain region of $\mathbf{k}$ -space is described through the distribution functions of the electrons, $f_e(\mathbf{k}, t)$ and holes, $f_h(\mathbf{k}, t)$. These distribution functions will evolve in time as charge carriers are generated, interact with one another and the lattice ions then relax back to the

equilibrium state of the material. Two different sets of equations are often utilised in the discussion of the time evolution of the carrier distribution functions. The semiconductor Bloch equations [11] are normally employed in the analysis of nonlinearities and coherent processes, which are often only important on sub-100 fs timescales. The Boltzmann equation [12] is in the case of drift-diffusion models when (nearly) static electric fields are present in the material and is typically used for timescales beyond 100 fs of photo-excitation. Due to the mathematical difficulty in solving these equations numerical techniques, such as the Monte Carlo method [13] are often employed. Another means of reducing the intractability of these equations is to separate the processes which relax the momentum of the carriers, such as carrier-carrier collisions, from the energy relaxation mechanisms, such as carrier-lattice interactions. This allows for a simpler discussion of the relaxation dynamics in terms of the average momentum, $\langle \mathbf{p} \rangle$, momentum relaxation time, τ_m , average energy, $\langle E \rangle$, and energy relaxation time, τ_E , of the carriers.

2.2.3.1 Laser Energy Distribution

Upon photo-excitation the energy distribution of charge carriers is radically altered from the equilibrium state of the semiconductor. The photo-generated energy distribution is determined primarily from the sum over all transition probabilities, which is a complex function of the material and excitation parameters, and the timescale of the excitation, as other processes may affect the evolution of this distribution even during carrier generation. Clearly, no general distribution function can be developed; nonetheless,

through careful analysis broad features of the energy distributions of the charge carriers can be discerned.

By nature, an ultrashort duration laser pulse has an associated broad spectrum in frequency space. The spectral distribution of the electric field of the pulse, $\mathbf{E}(\omega)$, is related to the time domain shape, $\mathbf{E}(t)$, through the Fourier relation:

$$|\mathbf{E}(\omega)| = \left| \int_{-\infty}^{\infty} \mathbf{E}(t) e^{-i\omega t} dt \right|. \quad (2.2.6)$$

Thus, the energy distribution of a pulse is simply the absolute value of the Fourier transform of the temporal pulse shape. The energy width of an arbitrary temporal shaped pulse (assuming it has not dispersed and is, therefore, transform limited) is given through the Fourier relation:

$$\Delta E \Delta \tau \approx hK, \quad (2.2.7)$$

where: $\Delta \tau$ is the temporal pulse duration of the full-width-at-half maximum (FWHM), ΔE is the energy FWHM, h is Planck's constant and K is a constant of order one which depends on the temporal shape of the pulse. Thus, the energy FWHM can be easily computed if the temporal duration and shape are well known.

2.2.3.2 Band Structure Considerations

The band structure of the material of study, in concert with the energy spectrum and central frequency of the excitation laser pulse, plays a crucial role in the determination of the charge carrier energy distributions. The energy separation of the three highest valence bands, shown in detail in Figure 2.2.3, allows discussion of the effect of illumination with an above band gap photon energy, E_i , to be split into two cases:

1) $E_l < E_g + \Delta E_{SO}$:

In this energy regime transitions may only occur from the hh-band to the CB and from the lh-band to the CB, as illustrated in Figure 2.2.3a. The excess energies of the electrons, $\Delta E_{e(h)}$, and holes, ΔE_h , can be calculated via equations 2.2.1a-c in terms of the fraction of excess energy above the band gap energy, $\Delta E_{exc} = E_l - E_g$:

$$\Delta E_{e(h)} = \Delta E_{exc} \frac{m_h^*}{m_e^* + m_h^*}, \quad (2.2.8a)$$

$$\Delta E_h = \Delta E_{exc} \frac{m_e^*}{m_e^* + m_h^*}, \quad (2.2.8b)$$

where: m_h^* is the effective mass of the heavy- or light-hole, and the notation, $\Delta E_{e(h)}$, stands for the excess energy due to a transition from hh- or lh-VB to the CB. For $|\mathbf{k}| \neq 0$, where the lh and hh bands are no longer degenerate, in order to satisfy energy conservation two populations of holes and two populations of electrons will exist in the VB and CB, respectively. One is a result of the hh $\rightarrow$ CB transition, producing electrons with excess energy, $\Delta E_{e(hh)}$, the other from the lh $\rightarrow$ CB transition, producing carriers with excess energy, $\Delta E_{e(lh)}$. As the electron and lh effective masses are similar in this energy regime for most III-V semiconductors, the electrons generated from a lh $\rightarrow$ CB transition and the light-holes will have nearly equal excess energy. This is not true for the hh $\rightarrow$ CB transition. Due to the larger radius of curvature of the hh-band over the CB and, therefore, much larger effective mass of the hh over the electron ($m_{hh}^* \sim 10m_e^*$) nearly all of the excess energy is attached to the electrons in the CB.

2) $E_l \geq E_g + \Delta E_{SO}$:

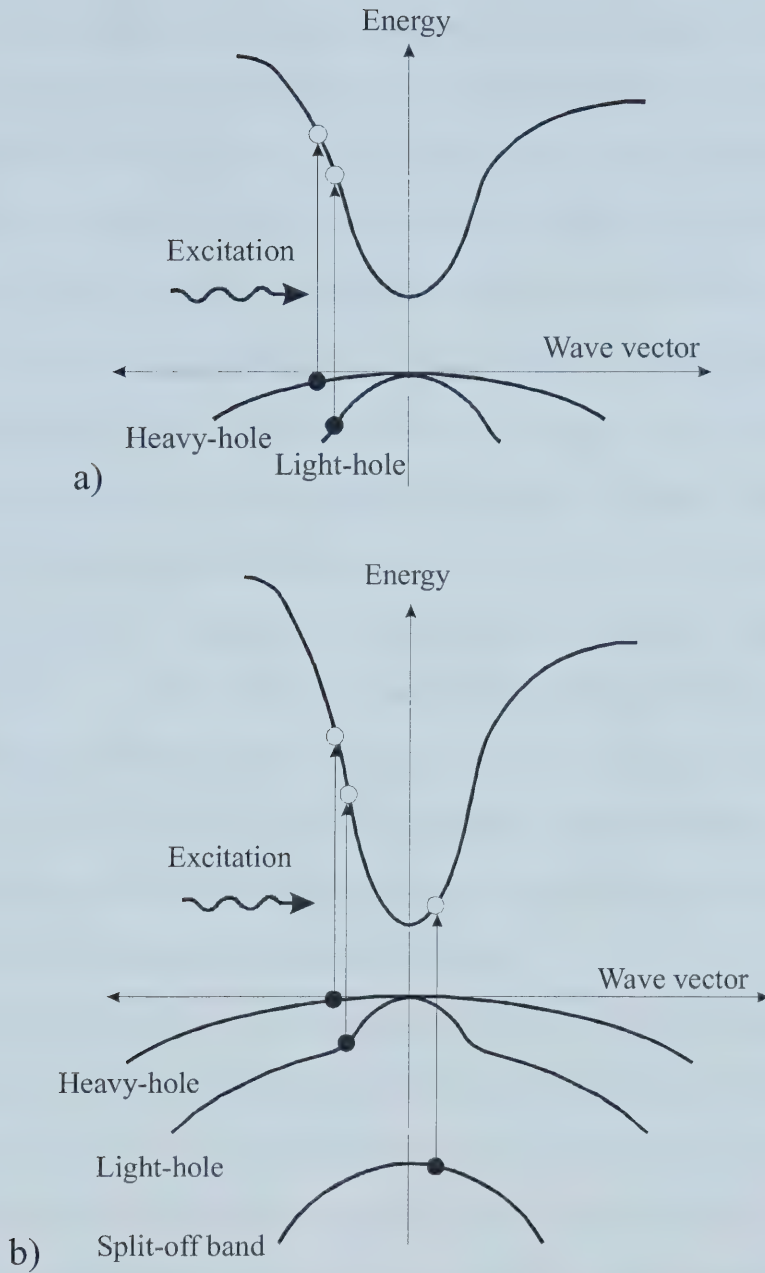


Figure 2.2.3. a) Two carrier populations produced during photo-excitation from the hh- and lh-bands to the conduction band, for photon energies below that necessary for an SO-band excitation. b) Three carrier populations produced upon photo-excitation from the hh-, lh-, and SO-bands to the conduction band.

If the excitation from the SO-band is also possible, the three different valence energy bands permit three different hole populations in the VB and three different electron populations in the CB, as seen in Figure 2.2.3b). In this regime, for $|\mathbf{k}|$ large, the lh-band has a similar curvature to the hh-band, albeit shifted down in energy by an amount, ΔE_{hh-lh} . Thus, heavy- and light-holes have very similar effective masses. The split-off hole, on the other hand, has an effective mass of $\sim 2-3 m_e^*$. Unfortunately, the non-parabolic nature of the CB and VB's in this energy range makes numerical calculations of excess energies much more difficult. For larger excess energies indirect (phonon-assisted) transitions to the L- and X-valleys of the CB may further cloud the picture. Normally, the phonon-assisted contribution to the excited populations is small as three body interactions (photon-carrier-phonon) are less probable than two body (photon-carrier) processes. At very high excitation levels ($E_l \sim$ a few eV) it may even be possible to excite higher conduction band levels.

Clearly, the nature of the multiple valence bands adds another level of complexity to the determination of the carrier energy distribution functions.

In addition to the laser energy parameters and material band structure, computation of the charge carrier energy distribution functions requires knowledge of the transition probabilities between VB and CB states. Calculation of the transition probabilities is normally accomplished via quantum mechanics and is inherently complex. A detailed treatment of transition probabilities is beyond the scope of this thesis and can be found in references 14 and 15. In general, the transition probability as a function of time is directly proportional to the incident laser intensity, $I(\omega)$, the joint density of states, $\rho(\omega)$, and the

percentage of those states which are available, in addition to a dependence on the wavefunctions of the initial and final states.

2.2.3.3 Transition Probabilities

As mentioned above, full calculation of the energy distributions of the electrons in the CB and holes in the VB is difficult as a result of the complexity of the transition probability. However, in the region near $|\mathbf{k}| = 0$ and for $E_l \approx E_g$ where the band structure is approximately parabolic a rough estimate can be made of the photo-excited carrier distributions. While the laser parameters are common, a feature which is unique for each of the heavy- and light-hole bands is the effective mass. In this region the total transition probability from the heavy- and light-hole bands to the conduction band can be approximated as [15]:

$$P_{vc}(t) \approx A_T(t) [\rho_{hh}(\omega) + \rho_{lh}(\omega)], \quad (2.2.9)$$

where: $\rho_{hh}(\omega)$ and $\rho_{lh}(\omega)$ are the heavy- and light-hole joint density of states, and $A_T(t)$ is a factor including all other (nearly) common terms. As the joint density of states is proportional to the 3/2 power of the effective mass for direct transitions [15] the hh contribution to the transition probability will be much larger than the lh. In this region of $\mathbf{k}$ -space the relative population densities due to the $lh \rightarrow CB$ transitions, W_{lh} , and from the $hh \rightarrow CB$ transitions, W_{hh} , can be written as:

$$W_{hh} = \frac{(\mu_{hh}^*)^{\frac{3}{2}}}{(\mu_{lh}^*)^{\frac{3}{2}} + (\mu_{hh}^*)^{\frac{3}{2}}}, \quad (2.2.10a)$$

$$W_{lh} = \frac{(\mu_{lh}^*)^{\frac{3}{2}}}{(\mu_{lh}^*)^{\frac{3}{2}} + (\mu_{hh}^*)^{\frac{3}{2}}}, \quad (2.2.10b)$$

where: μ_{lh}^* , μ_{hh}^* are the reduced masses ($\mu_{lh, hh}^* = (1/m_e^* + 1/m_{lh, hh}^*)^{-1}$) of the $lh \rightarrow CB$ and $hh \rightarrow CB$ transitions, respectively. Thus, the hh population will be larger than the lh population, owing to its greater effective mass. In GaAs this results in approximately 2/3 of the population consisting of heavy-holes and 1/3 of light-holes, at an excitation photon energy of $E_l = 1.51$ eV.

2.2.4 Charge Carrier Momentum Distribution

In a transient pump-probe reflectivity experiment, the probe beam measures the change in the occupation of the quantum states of a material within a specific energy region in $\mathbf{k}$ -space as a result of the pump beam excitation. In addition to occupying a specific energy state, the excited carriers also may have a momentum state, which can be measured by the probe pulse, thus, the momentum distribution of the charge carriers will affect the reflectivity measurement. In addition, as a result of crystal symmetry and quantum mechanics the polarization of the pump and probe beams may have a drastic affect on the detected momentum distribution.

The calculation of the momentum state of a carrier in the conduction band relies on the dipole approximation. In this approximation, for sufficiently small $|\mathbf{k}|$, the electron-hole system is treated as a dipole, with higher multi-pole contributions being neglected. The quantum mechanical calculation which is used to determine the transition probabilities between valence and conduction band states leads to rules on the spatial orientation of the dipole moments, hence, carrier momentum, $\hbar\mathbf{k}$, associated with a specific excitation. For excitation with linearly polarized above band gap energy radiation the momentum distribution of the carriers, $f_i(\mathbf{k})$, is found through [16,17]:

$$f_i(\mathbf{k}) = f_o(\mathbf{k})[1 + a_i P_2(\cos \theta)], \quad (2.2.11)$$

where: $P_2(\cos \theta)$ is the second Legendre polynomial, θ is the angle between the polarization vector of the excitation laser, $\mathbf{e}$, and the momentum of the charge carrier, $\mathbf{k}$, $f_o(\mathbf{k})$ is the symmetric part of the distribution function and a_i is the anisotropy parameter. For most III-V semiconductors, those similar to GaAs, the anisotropy parameter is $a_i = -1$ for the hh $\rightarrow$ CB transition, $a_i = +1$ for the lh $\rightarrow$ CB transition and $a_i = 0$ for the SO $\rightarrow$ CB transition. Figure 2.2.4 illustrates the momentum distributions with respect to the incident field corresponding to the different transitions. The hh $\rightarrow$ CB transition results in a $\mathbf{k}$ -space carrier distribution with momenta oriented primarily orthogonal to the excitation laser polarization, while the lh $\rightarrow$ CB transition generates a $\mathbf{k}$ -space carrier distribution with momenta oriented mostly parallel to the excitation laser polarization. In the case of a split-off band excitation the momenta are randomly oriented in $\mathbf{k}$ -space. In order to determine the total momentum distribution of the charge carriers the relative populations due to the three different VB $\rightarrow$ CB transitions must be known. Hence, the energy and momentum distributions are inexorably linked through the transition probabilities.

2.2.5 Energy and Momentum Redistribution

As seen in sections 2.2.3 and 2.2.4, the photo-generation of charge carriers in a semiconductor may result in a complex distribution of carriers in $\mathbf{k}$ -space. Once excited this distribution will eventually relax back to the equilibrium state through several processes which act to randomize the momentum/energy distribution, then reduce the total energy of the charge carriers. In general, the separate processes involved cannot be

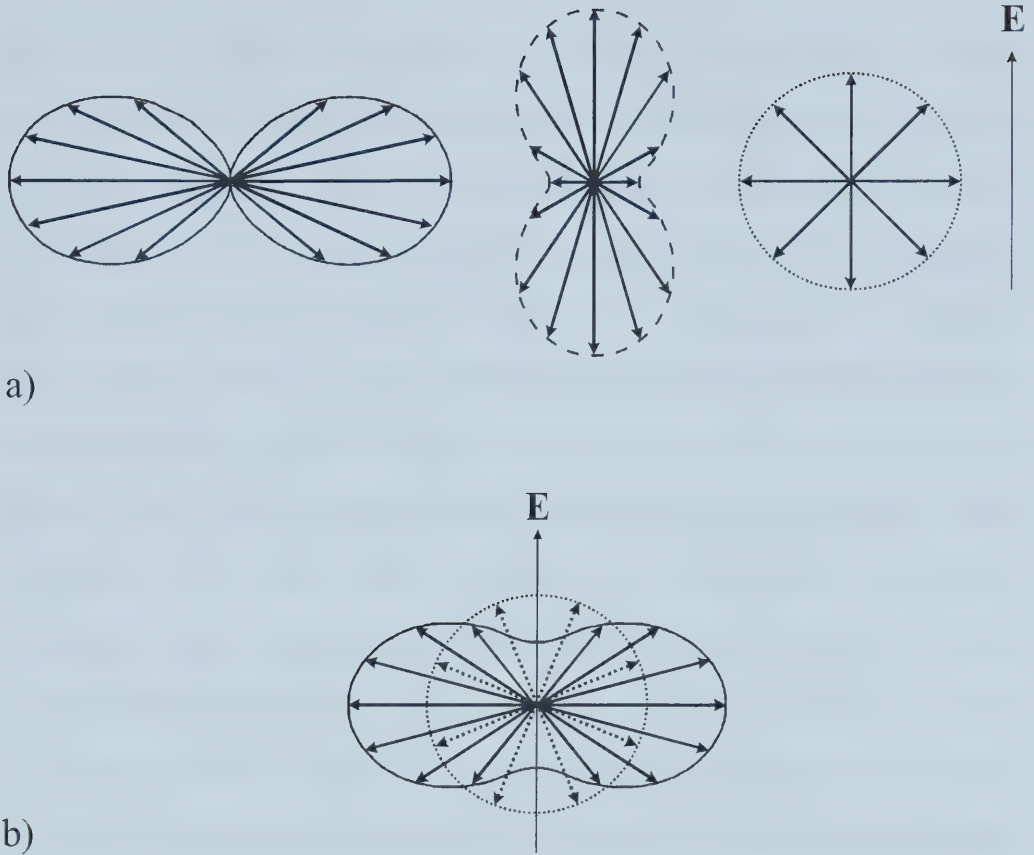


Figure 2.2.4. Momentum distributions of states in $\mathbf{k}$ -space resulting from photo-excitation of a zincblende semiconductor with a linearly polarized pump beam, $\mathbf{E}$. The arrows within the envelopes represent the magnitude and orientation of the momenta, $|\mathbf{k}|$, with respect to $\mathbf{E}$. a) The individual momentum distributions resulting from the heavy-hole (—), light-hole (- - -) and split-off band ($\cdot \cdot \cdot$) to CB transitions, as per equation 2.2.11. b) The net momentum distribution (—) resulting from a linearly polarized pump beam excitation at $E_p = 1.51$ eV in GaAs [17]. The isotropic distribution ($\cdot \cdot \cdot$) is shown for reference.

isolated in time as they occur simultaneously. Under certain circumstances the events which randomize the energy distribution but maintain the average energy of the carriers can be differentiated from those that reduce the average carrier energy. What follows is a brief introduction to the stages of carrier relaxation, with a more detailed description given in subsequent sections. Depicted in Figure 2.2.5 is a rough guideline for the phases in the temporal evolution of a carrier distribution function upon photo-generation by an ultrashort laser pulse. Initially, the shape of the carrier energy distribution is governed by the optical pulse shape and transition probabilities specific to the semiconductor under consideration. For a linearly polarized excitation this will also result in a preferential occupancy of specific momentum states, as per section 2.2.4, and is known as anisotropic state-filling (ASF) [18]. In this stage of carrier relaxation the electron and hole pair exist in a coherent state and carrier dynamics are described by the semiconductor Bloch equations [11]. Interactions soon destroy the coherence, within the momentum dephasing time, creating a nonequilibrium carrier distribution which cannot yet be characterized by a ‘temperature’. If pure momentum randomizing processes are involved the system is said to progress from anisotropic to isotropic state-filling in $\mathbf{k}$ -space, where the momentum distribution has become randomized. The further relaxation of the carriers towards quasi-equilibrium Fermi-Dirac or Maxwell-Boltzmann distributions, with an effective carrier temperature different from the lattice temperature, known as carrier thermalization, is governed by the Boltzmann transport equation. Later, the carriers interact with various phonons which equilibrates the carrier and lattice temperatures. As the carrier energy relaxes and all of the lowest states in the CB become occupied, band-

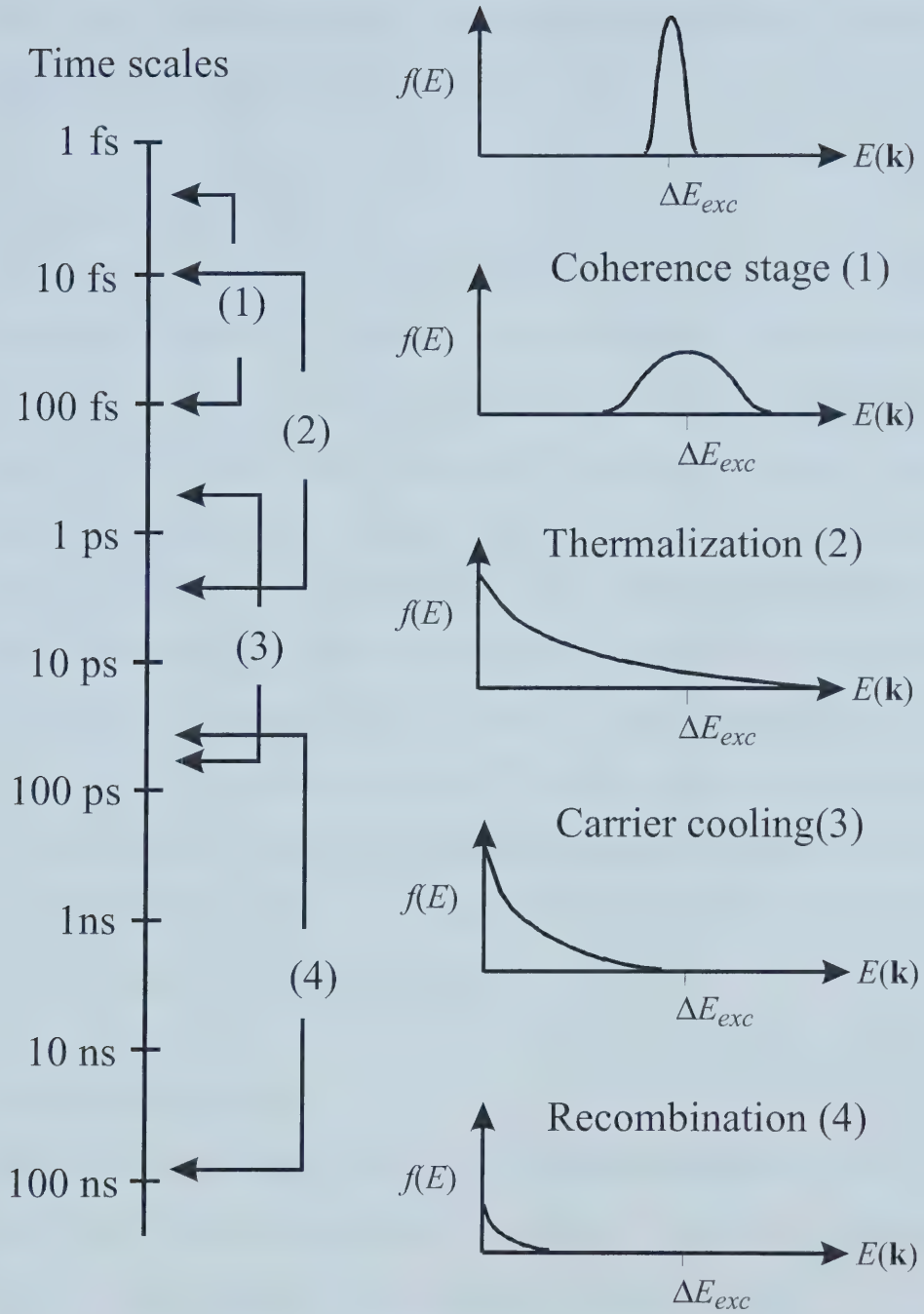


Figure 2.2.5. The stages in the time evolution of a charge carrier distribution after photo-excitation. The initial distribution is centred at an excess energy, ΔE_{exc}

filling is said to occur. In the final stage, the electrons and holes recombine, returning the material to the initial equilibrium state.

2.2.5.1 The Coherent State

The interaction of a photon of energy greater than E_g with a direct band gap semiconductor results in the generation of an electron-hole pair with special characteristics. This pair is locked in a coherent state and has a very specific dipole moment orientation [19,20], which is determined by quantum selection rules. Indirect band gap semiconductors do not have this coherent initial state as the participation of a phonon in the excitation acts as a randomizing agent. For excitation with a polarized laser source, a macroscopic dipole moment will be formed. In $\mathbf{k}$ -space this macroscopic dipole is manifested as a preferential filling of CB states of a given momentum orientation, resulting in ASF [18] and only lasts until the carriers begin to interact amongst themselves and the other elements in the crystal. In optical measurements the anisotropic nature of this process means that it is apparent through observation of third order nonlinearities in the material [18], as shall be seen in section 2.3.3.

2.2.5.2 Relaxation Processes

After photo-excitation and creation of the initial coherent state there are relatively few processes which act to alter the charge carrier distribution in $\mathbf{k}$ -space on sub-picosecond timescales. These processes can be grouped into three categories [18,21-23]:

- 1) *Processes which randomize momentum but do not alter the average carrier energy.*

This includes:

- a) Ionized impurity scattering.

This process will act purely to dephase the initially coherent carrier distribution, and will not act to thermalize the carriers.

- 2) *Processes which spread the carrier energy distribution as well as the momentum distribution but do not change the average carrier energy.*

This includes:

- a) Two particle carrier-carrier scattering between similar mass particles.

This process acts primarily to destroy the coherent phase but may also influence carrier thermalization in specific instances.

- 3) *Processes which modify carrier momentum and energy distributions as well as the average excess energy of the carriers.*

These include:

- a) Carrier-carrier scattering between dissimilar type carriers (e-hh, lh-hh) particles,
- b) Large $\mathbf{k}$ -vector phonon-electron scattering (a.k.a. intervalley scattering),
- c) Optical phonon-carrier scattering.

These processes affect every aspect of carrier redistribution, from causing a dephasing of the coherent state to bringing about carrier thermalization and, in the case of optical phonon-carrier scattering, effect carrier cooling to the lattice temperature.

Typically, pure momentum randomizing processes do not play an important role in the dynamics on sub-picosecond timescales. Ionized impurity scattering is highly dependent on the impurity concentration, which is quite low in the ultra pure semiconductors. Also, for increasing temperatures (i.e. above absolute zero) and large

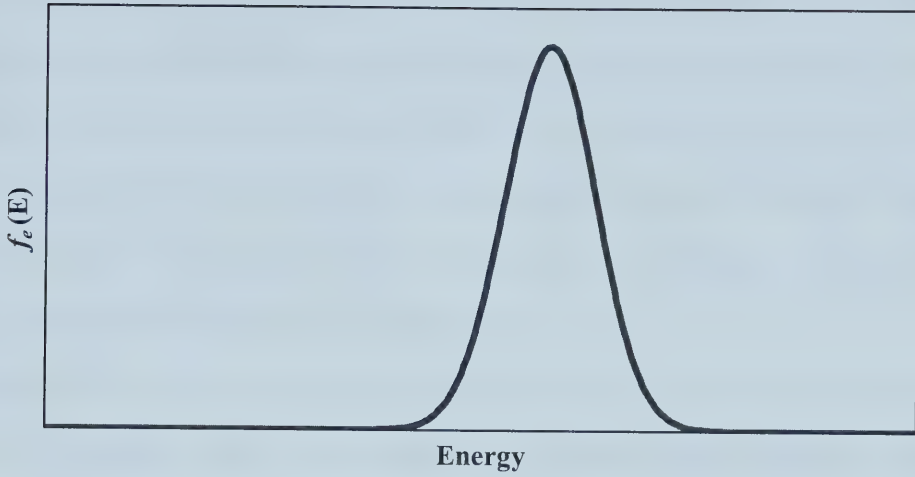
excess carrier energies the impurity scattering rates decrease and lose importance relative to the phonon scattering processes [22]. Thus, the role of impurity scattering in the distribution relaxation processes is small relative to other scattering events.

As previously mentioned, the act of photo-excitation may result in the creation of several distinct carrier distributions in the CB and VB. Under conditions of elastic scattering, interaction between carriers within each separate distribution (i.e. hh, lh or electron) cannot result in a change in the average energy of the distribution, only in the shape of the energy distribution function [23,24]. The effect of intra-distribution collisions on the non-equilibrium photo-generated carrier distribution is, therefore, to transform each like-carrier distribution (hh, lh or electron) into a quasi-equilibrium form. The exact form of this equilibrium distribution function depends on the excess carrier energy, the photo-injected carrier density and the density of states of the band. For very low excess energy excitations and/or large excited carrier densities the limited density of states near the CB minimum may result in total occupation of the lowest states upon carrier-carrier scattering, hence, a Fermi-Dirac-like distribution will form. For higher excess carrier energies or very low excitation levels the density of states will not be saturated, thus, a Maxwell-Boltzmann energy distribution may form. For moderate densities and excess energies a hybrid of the above mentioned distributions forms. Timescales for this local equilibrium to become established are difficult to predict as they vary according to number density and excess energy of the charge carriers and are often difficult to separate from the processes mentioned in point 3).

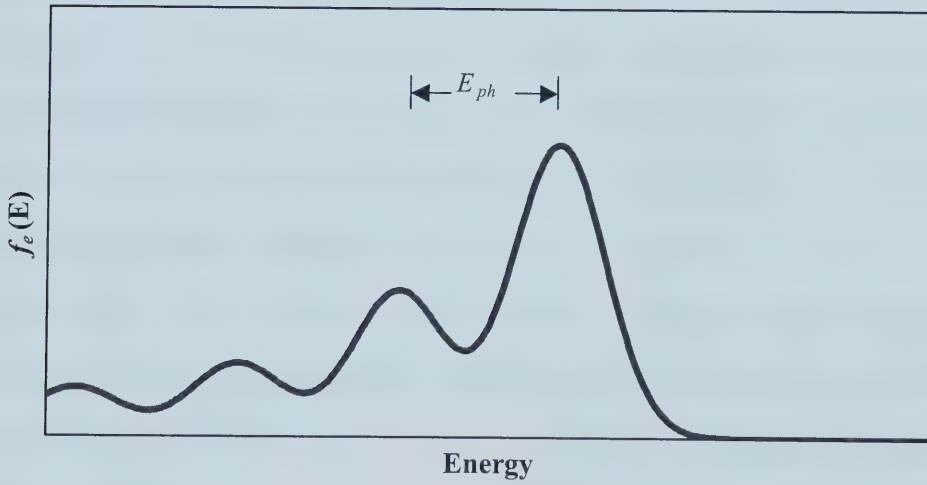
Several processes act to alter not only the momentum and energy distributions of the carriers but to also reduce the average carrier energy. In order to relax to the minimum of

the CB or maximum of the VB the carriers have to somehow lose their excess energy. In polar semiconductors, such as GaAs and InSb, on sub-picosecond timescales this is principally accomplished through the emission of a small $|\mathbf{k}|$ LO-phonon [23,24]. Energy conservation dictates that the carrier loses energy equal to the Γ -valley LO-phonon energy, typically $E_{LO} = 20\text{-}40$ meV. This process will occur until the excess carrier energy is small enough such that energy conservation forbids LO-phonon emission. The effect of this process on the energy distribution function of the carriers can be seen in Figure 2.2.6. The initial distribution, Figure 2.2.6a, is replicated at energy intervals equal to the phonon energy, Figure 2.2.6b. As with most carrier relaxation processes LO-phonon assisted energy relaxation is carrier density dependent and the interaction may be screened at large carrier densities [22]. Another high density effect which limits carrier cooling is known as the phonon-bottleneck effect [23], whereby the emission rate of LO-phonons by the carriers becomes approximately equal to the LO-phonon re-absorption rate. In the absence of screening or phonon-bottleneck effects, the timescales for the onset of the phonon interaction would be expected to be on the order of the phonon period, $\tau_{LO} \sim 100\text{-}200$ fs.

Once the carriers have relaxed below the LO-phonon emission energy the carrier distribution may further relax through acoustic phonon emission. However, on sub-picosecond timescales acoustic phonon scattering does not normally contribute to the carrier cooling process. This is a result of the small energy (hence, low frequency) of a Γ -valley acoustic phonon which implies a correspondingly long interaction time, typically on the order of 1-10 ps.



a)



b)

Figure 2.2.6. The evolution of the distribution function as a result of LO-phonon emission, after reference 23. a) The initial distribution function. b) Replicas of the distribution are created, spaced in energy by the phonon energy, E_{ph} .

Another means by which a specific carrier distribution can lose excess energy is through interactions with other carrier distributions [23, 25]. For incident photon energies above E_g , several electron and hole energy distributions may be created (Figure 2.2.3). As a result of the effective mass differences between the electrons, heavy- and light-holes, each distribution will have a different average energy (see equations 2.2.8a and 2.2.8b). Thus, the inter-carrier distribution collisions will result in a redistribution of the average energy of each of the individual carrier distributions.

Upon photo-excitation the electron and hole distributions may evolve in the following manner: Initially, the carriers are generated into well defined energy distributions. Intra- and inter-carrier distribution interactions commence, which alters the average energy and shape of the energy distributions. Typically, for excitation below the SO-band excitation threshold, the effect is to reduce the average energies of the electron and lh distributions while the hh distribution will experience an increase in the average energy, as a result of the large mass difference between the heavy-holes and light-holes or electrons. LO-phonon emission results in further energy relaxation, creating distribution replicas separated by the LO-phonon energy [23]. The processes of carrier-carrier collision and LO-phonon emission continue until all carriers are below the LO-phonon emission threshold or all the lowest states in the CB or highest states in the VB become filled. While the LO-phonon emission process does facilitate the relaxation of the carriers to the band minima it is not a necessary component for energy relaxation. In the case where none of the carriers have excess energies exceeding the LO-phonon emission threshold (very near band edge photo-excitation) the carrier distributions will equilibrate through carrier collisions into quasi Fermi-Dirac distributions. On long timescales acoustic

phonon emission will relax the non-thermal carriers to the band edge. Pure carrier-carrier scattering times show a strong density dependence [16,17] and may occur on timescales as short as a few tens of femtoseconds.

Another carrier energy distribution non-conserving event is illustrated in Figure 2.2.7. For large excess electron energies in the Γ -valley, the interaction of a carrier with a large wave vector phonon can result in the carrier being scattered to the L- or X-conduction band valleys, as per the excess energy of the carrier. This may occur on sub- 50 fs timescales [13, 26-28] while the remaining Γ -valley population may only be a fraction of the initially excited number density. As the populations in the CB relax towards the bottom of their respective valleys, the probability of the carriers scattering back into the Γ -valley increases over scattering into the side valleys. Hence, on picosecond timescales the side valleys are depopulated and the carriers thermalize in the Γ -valley. Clearly, the effect of side valley scattering is to reduce the energy relaxation rate.

2.3 Reflectivity Measurement: Theory

Interpretation of transient pump-probe reflectivity data requires an understanding of both the basic mechanisms that occur in semiconductors on sub-picosecond timescales as well as the mathematical tools necessary to extract that information. The first section will discuss the important parameters which shape the spectral components of a reflectivity signal. This is followed by a treatment of the terms linear and nonlinear in the optical field that are relevant to pump probe measurement. A time domain picture is then presented, concluding with a specific example of how a temporal reflectivity signal is related to the material response through the third order polarization and the form of the

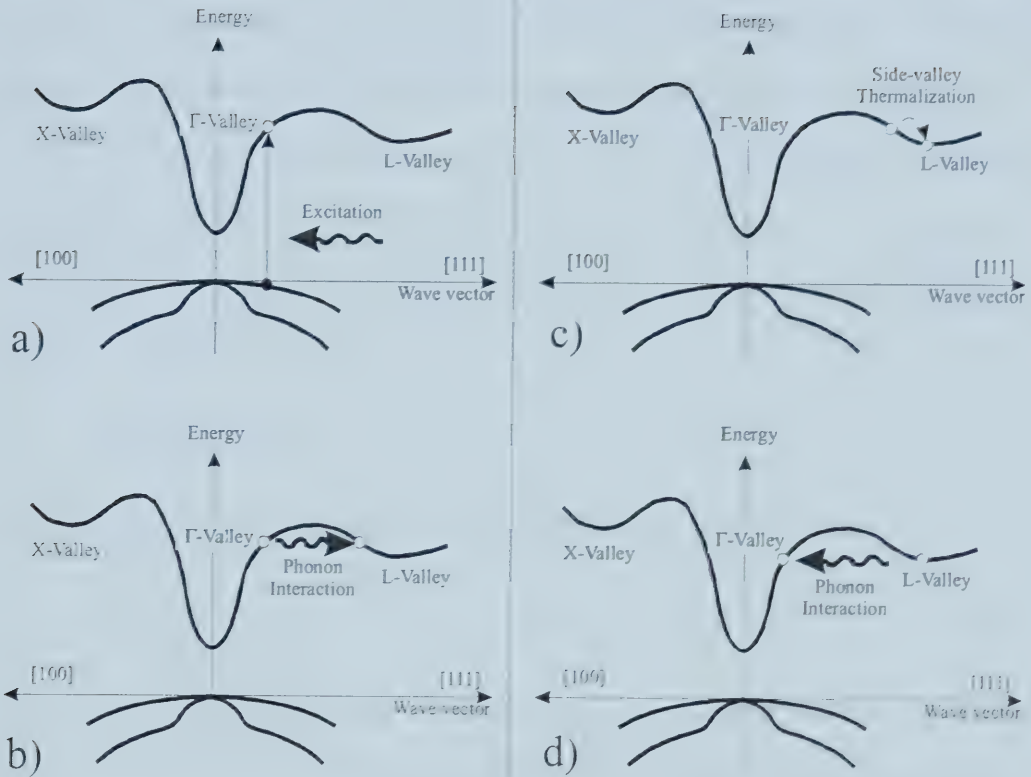


Figure 2.2.7. Band diagram representation of intervalley electron-phonon scattering. a) A carrier is excited with a large amount of excess energy. b) The carrier interacts with a phonon and scatters to the L-valley. c) The electron relaxes within the L-valley. d) Scattering back into the Γ -valley.

optical fields present.

2.3.1 Mathematical Formalism

Transient pump-probe reflectivity studies rely on the interaction of the probe intensity with the semiconductor under study. Upon reflection the measured intensity is altered, and evolves as the temporal delay between the pump and probe beams is varied. This measured reflected intensity change is due to variations in the dielectric function and polarization state of the material. The change in reflectivity, ΔR , can be expressed in terms of the complex index of refraction, $n_c = n + ik$, through the real index of refraction, n , and the extinction coefficient, k :

$$\Delta R \approx \frac{\partial R}{\partial n} \Delta n + \frac{\partial R}{\partial k} \Delta k, \quad (2.3.1)$$

where the reflected intensity coefficient for normal incidence takes the form:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (2.3.2)$$

in a material exhibiting absorption. The change in reflectivity divided by the reflected intensity coefficient (referred to the differential or change in reflectivity) then becomes:

$$\frac{\Delta R}{R} = A_R \Delta n + 2B_R \Delta k, \quad (2.3.3a)$$

where:

$$A_R = \frac{4(n^2 - k^2 - 1)}{[(n+1)^2 + k^2][(n-1)^2 + k^2]}, \quad (2.3.3b)$$

$$B_R = \frac{4nk}{[(n+1)^2 + k^2][(n-1)^2 + k^2]}. \quad (2.3.3c)$$

Through the causal nature of material response to electromagnetic fields, a relationship exists between the real and imaginary parts of $\varepsilon(\omega)$ and can be expressed through the Kramers-Kronig relations. As the complex index of refraction, $n_c(\omega)$, is related to the dielectric function via $\varepsilon(\omega) = n_c^2(\omega)$, its real, $n(\omega)$, and imaginary, $k(\omega)$, parts must also be related via the Kramers-Kronig relations. Since the extinction coefficient is directly proportional to the absorption coefficient, $\alpha(\omega)$:

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda}, \quad (2.3.4)$$

the change in the index of refraction, as a function of frequency, $\Delta n(\omega)$, can be written in terms of the change in absorption, $\Delta\alpha(\omega)$ [7]:

$$\Delta n(\omega) = \frac{c}{\pi} \int_0^{\infty} \frac{\Delta\alpha(\omega')}{(\omega')^2 - \omega^2} d\omega', \quad (2.3.5)$$

where: c is the speed of light. Equation 2.3.5 along with equation 2.3.4 can be substituted into equation 2.3.3a to generate an expression for the change in reflectivity solely in terms of the absorption as a function of frequency:

$$\frac{\Delta R(\omega)}{R} = A_R \frac{c}{\pi} \int_0^{\infty} \frac{\Delta\alpha(\omega')}{(\omega')^2 - \omega^2} d\omega' + B_R \frac{c}{\omega} \Delta\alpha(\omega). \quad (2.3.6)$$

This relation is central to the interpretation of pump-probe reflectivity measurement as the material process which occur upon pump beam excitation are most easily expressed in terms of a change in absorption.

For optical measurement at a photon energy just above or below the band gap of the semiconductor under study, often the extinction coefficient will satisfy the condition, $k \ll n - 1$. In such instances the extinction coefficient, k , is normally neglected relative to

the real part of the index of refraction, n . This leads to a simpler form of the reflectivity response equation:

$$\frac{\Delta R}{R} = \frac{4\Delta n}{n^2 - 1}, \quad (2.3.7)$$

or, in terms of the change in absorption:

$$\frac{\Delta R(\omega)}{R} = A_R' \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega')}{(\omega')^2 - \omega^2} d\omega', \quad (2.3.8a)$$

with:

$$A_R' = \frac{4}{(n^2 - 1)}. \quad (2.3.8b)$$

Equation 2.3.7 is considerably simpler to deal with in certain instances, when the change in the index of refraction is known explicitly rather than the absorption.

2.3.2 Nonlinearity in Reflectivity Measurement

The application of the pump and probe electric fields to a material of study in a transient reflectivity experiment clearly acts to alter the properties of said material. For low field amplitudes and/or for certain frequency ranges the response of a dielectric medium to an electric field can be written in terms of a linear relation, through the polarization:

$$P_i^{(1)}(\omega) = \epsilon_o \chi_{ij}^{(1)}(\omega) E_j(\omega), \quad (2.3.9)$$

where: $\chi_{ij}^{(1)}(\omega)$ is the first order susceptibility and $P_i^{(1)}(\omega)$ is the polarization in the i^{th} direction (x, y or z). For larger fields or near resonances, such as the band gap energy in a

semiconductor, the relationship between the electric field and polarization may become nonlinear, and can be stated through the well known relation:

$$\mathbf{P}(\omega) = \mathbf{P}^{(1)}(\omega) + \mathbf{P}^{(2)}(\omega) + \mathbf{P}^{(3)}(\omega) + \dots, \quad (2.3.10)$$

$$P_i = \epsilon_o \left[\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \right], \quad (2.3.11)$$

where: $E_j(\omega_n)$ is the j^{th} component of the field with frequency ω_n , $\chi_{ijk}^{(2)} = \chi_{ijk}^{(2)}(\pm\omega_1 \pm \omega_2; \omega_1, \omega_2)$ is the second order susceptibility, $\chi_{ijkl}^{(3)} = \chi_{ijkl}^{(3)}(\pm\omega_1 \pm \omega_2 \pm \omega_3; \omega_1, \omega_2, \omega_3)$ is the third order susceptibility and the frequency arguments in equation 2.3.11 have been dropped for brevity.

Two important material response characteristics can be observed from the form of equation 2.3.11. First, the tensor character of the optical susceptibilities indicates that the polarization state of the incident optical field may play an important role in the nature of the material response. Secondly, even order susceptibilities do not produce a response at the frequency of the incident field as the polarization response occurs at the sum and difference frequencies of the fields which make up the polarization term. In a pump-probe experiment where both pump and probe beams originate from the same source this implies the second order polarization response occurs at either the second harmonic frequency ($\omega + \omega = 2\omega$) or at DC ($\omega - \omega = 0$). Thus, even order terms do not contribute to pump-probe experimental measurement at the frequency of the incident fields, ω .

With the above formalism the dielectric function of the medium exhibiting a nonlinear response, $\epsilon'(\omega)$, can now be expanded in terms of the susceptibilities. Thus, treating the susceptibilities and fields as scalars, for simplicity, and keeping terms up to third order [29]:

$$\varepsilon'(\omega) = \varepsilon_o \left(1 + \chi^{(1)} + \chi^{(3)} |\mathbf{E}|^2 \right), \quad (2.3.12a)$$

$$\varepsilon'(\omega) = \varepsilon(\omega) + \varepsilon_3(\omega). \quad (2.3.12b)$$

where: $\varepsilon(\omega) = \varepsilon_o (1 + \chi^{(1)})$ is the first order approximation to the dielectric function, $\varepsilon_3(\omega) = \varepsilon_o \chi^{(3)} |\mathbf{E}|^2$, and the second order susceptibility term has been excluded from equations 2.3.12a and 2.3.12b as it is not relevant in pump-probe measurements. As for the dielectric function, the real index of refraction, $n'(\omega)$, and the absorption coefficient, $\alpha'(\omega)$, in a nonlinear medium can be expanded in a series in the applied field. Including only terms in the intensity of the field:

$$n'(\omega) = n(\omega) + \Delta n_{NL}(\omega) = n(\omega) + n_2(\omega) I(\omega), \quad (2.3.13a)$$

$$\alpha'(\omega) = \alpha(\omega) + \Delta \alpha_{NL}(\omega) = \alpha(\omega) + \tilde{\beta}(\omega) I(\omega), \quad (2.3.13b)$$

where: $n(\omega)$ is the linear index of refraction, $\alpha(\omega)$ is the linear absorption coefficient, $I(\omega)$ is the intensity of the incident electric field, $n_2(\omega)$ and $\tilde{\beta}(\omega)$ are the nonlinear coefficients. For an electric field which interacts with the material the complex propagation vector, $\kappa(\omega)$, of the field will depend on the dielectric function. In the approximation that the nonlinearity is weak:

$$\kappa(\omega) = \omega \sqrt{\mu \varepsilon'(\omega)}, \quad (2.3.14a)$$

$$\approx \omega \sqrt{\mu \varepsilon(\omega)} \left(1 + \frac{\Delta \varepsilon_R(\omega)}{2 \varepsilon(\omega)} - i \frac{\Delta \varepsilon_I(\omega)}{2 \varepsilon(\omega)} \right), \quad (2.3.14b)$$

where: $\varepsilon_3(\omega)$ has been expanded into its real, $\Delta \varepsilon_R(\omega)$, and imaginary, $\Delta \varepsilon_I(\omega)$, parts. For weak absorption, such that $\varepsilon(\omega)$ is predominantly real the propagation vector can be rewritten in a more evocative manner:

$$\kappa(\omega) \approx \frac{2\pi n(\omega)}{\lambda} + \frac{2\pi \Delta n_{NL}(\omega)}{\lambda} - i \Delta \alpha_{NL}(\omega). \quad (2.3.15)$$

The first term corresponds to the expected form of the propagation vector in a dispersionless medium. However, the second term appears similar to a phase shift resulting from the nonlinear properties of the medium, while the last term appears similar to the nonlinear change in the absorption properties of the medium. In general the n^{th} order susceptibility, like the dielectric function, is a complex quantity having real, $\chi_R^{(n)}$, and imaginary, $\chi_I^{(n)}$, components. Therefore, the following identifications can be made [29]:

$$\Delta n_{NL}(\omega) = \frac{1}{2n(\omega)} \chi_R^{(3)} E^2, \quad (2.3.16a)$$

$$\Delta \alpha_{NL}(\omega) = \frac{\pi}{\lambda n(\omega)} \chi_I^{(3)} E^2. \quad (2.3.16b)$$

In a differential reflectivity experiment which measures the nonlinear response of a medium, the change in the index of refraction, Δn , can be written in terms of a linear term, Δn_L , and a nonlinear term, Δn_{NL} . Therefore, equation 2.3.7 can be cast in the form:

$$\frac{\Delta R}{R} = \frac{\Delta R_L}{R} + \frac{\Delta R_{NL}}{R}, \quad (2.3.17a)$$

$$= \frac{4}{n^2 - 1} (\Delta n_L + \Delta n_{NL}), \quad (2.3.17b)$$

$$= \frac{4}{n^2 - 1} \left(\Delta n_L + \frac{\chi_R^{(3)} E^2}{2n} \right). \quad (2.3.17c)$$

Thus, in the frequency domain the differential reflectivity signal is governed by both the real part of the complex index of refraction and the real part of the third order susceptibility. This is in contrast to transmission experiments where the imaginary part of the complex index of refraction, which is directly proportional to the absorption, and imaginary portion of the third order susceptibility are primarily responsible for the

observed signal variations [30]. As such, much of the formalism developed for transmission can be readily applied to reflectivity measurement, with $\chi_R^{(3)}$ used in place of $\chi_I^{(3)}$.

2.3.3 Time Domain Formalism

While the discussion in the previous section was confined to the frequency domain, in order to model the temporal behaviour of a transient pump-probe reflectivity signal this information must be transferred to the time domain. The optical susceptibility can be related to the time domain material response via a Fourier transform [31]:

$$\chi_{ijkl}^{(3)}(\omega_1 + \omega_2 + \omega_3; \omega_1, \omega_2, \omega_3) = \int_0^\infty \int_0^\infty \int_0^\infty R_{ijkl}(t', t'', t''') e^{i(\omega_1 t' + \omega_2 t'' + \omega_3 t''')} dt' dt'' dt''', \quad (2.3.18)$$

where: $R_{ijkl}(t', t'', t''')$ is the material response. This relation demonstrates that the time domain material response will be limited by the same symmetry considerations as the third order susceptibility. In addition, this implies a direct relation between the differential reflectivity, equation 2.3.17c, and the material response.

In a publication by Z. Vardeny and J. Tauc [30], a mathematical treatment of a transient pump-probe transmission experiment in the time domain, based on the third order polarization induced in the material, is formulated. Initially, a medium exhibiting a third order polarization response of the form:

$$P_i(\mathbf{r}, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_{ijkl}(\mathbf{r}, t-t', t-t'', t-t''') E_j(\mathbf{r}, t') E_k^*(\mathbf{r}, t'') E_l(\mathbf{r}, t''') dt' dt'' dt''', \quad (2.3.19)$$

is assumed. Here, the material response is proportional to the imaginary part of the third

order susceptibility [30]. Then, the resultant change in transmitted intensity of the probe beam due to the third order polarization, as measured by a photo-detector is found to be:

$$\Delta I = A_I \int_S ds \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_i^*(\mathbf{r}, t) E_j(\mathbf{r}, t) R_{ijkl}(t-t') E_k^*(\mathbf{r}, t') E_l(\mathbf{r}, t') dt dt', \quad (2.3.20)$$

where: A_I is a constant, S is the area of the detector illuminated by the transmitted beam and summation over i, j, k , and l is assumed. In this picture the total field at the sample, $\mathbf{E}_T(\mathbf{r}, t)$, will be a combination of the pump and probe field amplitudes:

$$\mathbf{E}_T(\mathbf{r}, t) = \mathbf{E}_1(t) e^{i\mathbf{k}_1 \cdot \mathbf{r}} + \mathbf{E}_2(t) e^{i\mathbf{k}_2 \cdot \mathbf{r}}. \quad (2.3.21)$$

where: $\mathbf{k}_1$ and $\mathbf{k}_2$ are the propagation vectors of the pump and probe beam, respectively. Here, only terms for which the total radiated field propagates in the direction of the detector will be observed. After integration over illuminated detector area, the signal becomes:

$$\Delta I = AS \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_i^*(t) E_j(t) R_{ijkl}(t-t') E_k^*(t') E_l(t') dt dt'. \quad (2.3.22)$$

In order to further simplify the form of equation 2.3.22 an understanding of the different combinations of field amplitudes which affect the signal must be reached. Typically, the probe beam is assumed to be the delayed, less intense image of the pump beam:

$$|\mathbf{E}_2(t)| = b |\mathbf{E}_1(t-\tau)|, \quad b \ll 1. \quad (2.3.23)$$

In addition, only certain combinations of fields can produce a response in the direction of the probe beam and at the same frequency, ω , as the probe field. Thus, two probe field components and two pump field components must be present in equation 2.3.22. For linearly polarized pump and probe beams the summation implicit in equation 2.3.22 can

be carried out and the transmitted intensity measured by the detector as a function of pump-probe delay time becomes:

$$\Delta I(\tau) = \gamma(\tau) + \beta(\tau), \quad (2.3.24)$$

with:

$$\gamma(\tau) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |E_m(t-\tau)|^2 R_{mmp} (t-t') |E_p(t')|^2 dt' dt, \quad (2.3.25a)$$

$$\beta(\tau) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_m^*(t-\tau) E_p(t) R_{mppm} (t-t') E_p^*(t') E_m(t'-\tau) dt' dt. \quad (2.3.25b)$$

In equations 2.3.25a and 2.3.25b the subscripts on the field components and the material response function are used to indicate the pump (p) and probe (m) polarizations, which may be either parallel ($p = m = x$ -direction) or perpendicular ($p = y, m = x$). As a result of the discussion at the end of the section 2.3.2, the above equations are equally suited to model the differential transmission and reflectivity, with the material response being related to the imaginary part of $\chi^{(3)}$ in the case of transmission and the real part of $\chi^{(3)}$ in the case of reflectivity measurement.

Each of the terms in the measured intensity, hence, reflectivity or transmittivity response are a result of different effects [32]. The $\gamma(\tau)$ term is known as the population term and is a result of the anticipated dynamical behaviour measured in a pump-probe experiment. Here, the pump intensity generates a real population, such as charge carriers in a semiconductor, which modifies the reflected intensity of the probe beam. The second term, $\beta(\tau)$, known as the polarization coupling term, is of a significantly different origin. In this case, the pump and probe field coherence causes an induced grating to form, which scatters the pump light in the direction of the probe beam. This grating exists only

as long as the pump and probe fields overlap in time and its nature depends sensitively on the relative pump and probe beam polarizations. For parallel polarizations of the pump and probe beam the interference creates a real spatial population grating in the material of study. This alteration of the material properties, hence, the dielectric function in a periodic fashion serves as the grating from which the pump field scatters. For non-collinear orthogonally polarized pump and probe beams, at the surface of the sample the polarization state will vary with position in a periodic manner. In a semiconductor, as the final momentum state to which a carrier is excited depends on polarization (ASF), the momentum state of the carriers will form an orientational grating within the illumination spot [18]. This will act to scatter the pump beam in the probe direction, as the material properties, hence, dielectric function are once again periodically modified. The polarization coupling term is also known as the ‘coherent artefact’ and creates a symmetric peak centred about the zero time, as observed in many pump-probe experiments.

Equations 2.3.25a and 2.3.25b serve as the starting points for modeling of sub-picosecond time-resolved reflectivity and transmission experiments. Typically, a measured reflectivity signal in such an experiment can be determined solely from these equations, such that:

$$\frac{\Delta R(\tau)}{R} = \tilde{A}[\chi(\tau) + \beta(\tau)], \quad (2.3.26)$$

where: $\tilde{A}$ is a proportionality constant. Unlike equation 2.3.17c, which contains a linear and a nonlinear component to the reflectivity signal and describes the signal for all time, on sub-picosecond timescales the differential reflectivity will often follow the form given in equation 2.3.26. The dynamics which occur primarily result from the evolution of the

photo-generated carrier population ($\gamma(\tau)$ term), hence, are well described by the nonlinear version of the differential reflectivity. On longer timescales, such as when lattice heating becomes important, terms linear in the refractive index may have to be included.

2.4 Temporal Resolution Considerations

When dealing with laser pulses on the order of a few femtoseconds in duration there are several effects that can act to severely lengthen the pulse duration. In order to maintain the pulse duration and observe events such as the initial photo-generated charge carrier interactions in a semiconductor it is imperative that these sources of pulse spreading be either removed or compensated for. The purpose of the following sections is to discuss the main optical effects that act to increase the pulse duration: group velocity dispersion, spherical aberration, chromatic aberration and angular pulse broadening.

2.4.1 Group Velocity Dispersion

Fourier analysis indicates that an optical pulse with a given temporal duration will have a corresponding energy spectrum, as per equation 2.2.13. This can be re-formulated in terms of wavelength:

$$\frac{c}{\lambda_o^2} \Delta\lambda \Delta t \approx K, \quad (2.4.1)$$

where: Δt is the temporal duration, $\Delta\lambda$ is the wavelength spectral width, and λ_o is the central wavelength of the pulse. Transform limited pulses produced by passively-mode-locked Ti:Sapphire lasers typically have K values between 0.315 (for hyperbolic secant squared intensity with time) and 0.42 [33], while pulses which are Gaussian in time typically have $K = 0.441$ [32]. For a hyperbolic secant pulse with $\Delta t = \tau_p = 10$ fs, centred

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A final qualifying comment should be made with regard to equation 2.4.3. For sub-15 fs pulses the 2nd order approximation is too restrictive and does not fully express the functional form of the pulse spreading. Therefore, 3rd or even 4th order dispersive terms must be included in detailed calculations of the effects of temporal pulse broadening.

2.4.2 Chromatic and Spherical Aberration

Two other pulse broadening mechanisms exist which are inherent to the nature of most optical focusing elements. The first effect is a consequence of the paraxial approximation for which spherical focusing elements are only aberration free if illuminated within a narrow region near the centre of the optical element. This results in a shorter focal length for rays incident further from the centre of the focusing element and is known as spherical aberration. The second effect, occurring for refractive optics, is due to the wavelength dependent index of refraction leading to a wavelength dependent focal length, and is known as chromatic aberration.

The theory behind chromatic and spherical aberration induced pulse broadening mechanisms is conceptually easy but mathematically difficult [35,36]. As a result of these effects the pulse duration becomes a complex function of the optical parameters, such as lens diameter, focal length, illumination wavelength, and fraction of the lens illuminated. In addition, the duration of an optical pulse will have a spatial dependence, both in terms of the position from the focusing element and across the spatial intensity profile of the beam. While absolute quantification of the pulse duration is exceptionally difficult it is clear that both chromatic and spherical aberration will have an adverse influence on the temporal resolution if spherical refractive focusing elements are used.

2.4.3 Angular Pulse Broadening

The previously mentioned effects all have one thing in common, they are due to light propagation through a material which has dispersive or refractive properties. Unlike GVD, chromatic and spherical aberration, the effects of angular pulse broadening (APB) result from purely geometric considerations. Figure 2.4.1 illustrates the standard way in which APB manifests. In many experiments, in order to measure the intensity of the probe beam it must strike the sample at an angle relative to the sample normal, θ , while the pump beam is incident directly along the sample normal. As a consequence, the probe pulse front along the inside edge (A) will strike the sample sooner than the outside edge (B). The delay between arrival times of the inside and outside edges of the pulse front, τ_{APB} , can be calculated simply as:

$$\tau_{APB} = \frac{2w \sin(\theta)}{c}, \quad (2.4.5)$$

where: w is the probe beam radius at the sample. For a spot radius of $w = 5 \mu\text{m}$ and an incident angle of $\theta = 15^\circ$, the resultant delay between pulse front arrival times at points A and B will be $\tau_{APB} = 7.8 \text{ fs}$. Thus, the effect of APB on an output pulse of duration $\tau_p = 10 \text{ fs}$ is to broaden the measurement resolution to $\tau_p = 17.8 \text{ fs}$.

Interchanging the role of the pump and probe beams in this situation, so that the probe beam strikes the sample at normal incidence and the pump beam is incident at an angle, may not entirely solve this problem. While the resolution of the probe beam will be maximized, the pump beam will now see the effects of APB. As the pump spot is generally larger than the probe spot at the sample, the pump beam will undergo a larger pulse broadening. This may lead to a spatial dependence to the temporal evolution of the material changes induced by the pump beam. On ultrashort timescales, before effects

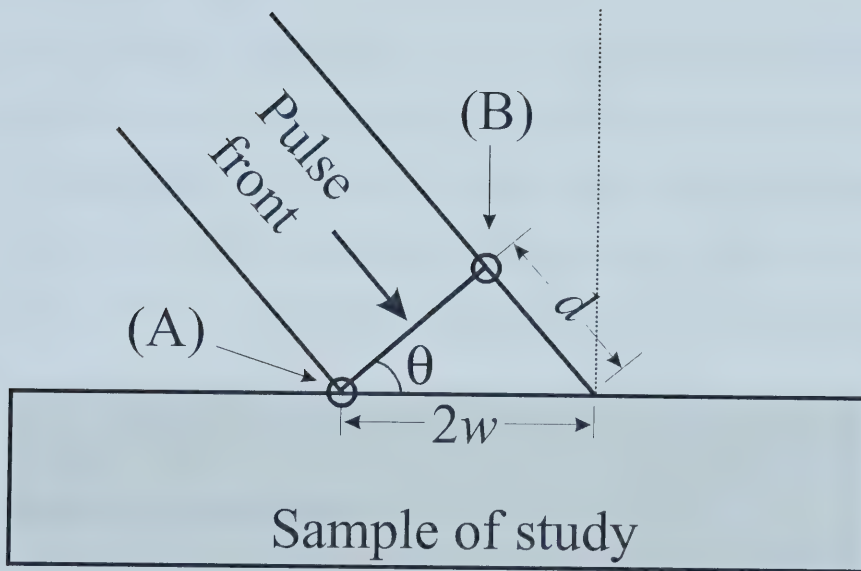


Figure 2.4.1. Geometrical considerations for pulse broadening due to a non-zero angle of incidence. The portion of the pulse from at point A strikes the sample before the portion at point B. The measured spot diameter, $2w$, is indicated.

such as charge carrier diffusion or field-induced drift can effectively homogenize the population within the probe spot region, the probe beam will measure a temporal average of these changes occurring within the area probed. The effective reduction in temporal resolution on short timescales will be the same as calculated previously, with w being the radius of the probe spot and θ being the angle at which the pump beam strikes the sample relative to the surface normal.

In order to induce events such as plasmon or coherent phonon oscillations, the generating mechanism (i.e. pump pulse) must have a shorter duration than a single period of the oscillatory motion. The duration of the pump pulse, in this case, is determined entirely by the diameter and incident angle of the pump pulse. Clearly, APB must be considered so as the pump pulse duration is sufficiently short so as to incite the event one wishes to observe.

2.4.4 Reducing Dispersive Effects

The observation of events via pump-probe experimental techniques on ultrashort timescales necessitates the careful management of both the pump and probe pulse durations. As such, many methods are used to combat the influence of GVD, angular dispersion, spherical and chromatic aberration, some more successful than others. The following discussion gives an overview of the different methods, their positive attributes and their drawbacks.

One of the more common ways to remove GVD in an experimental system is to place an optical element into the beam path that has tuneable dispersion characteristics of opposite sign to the total dispersion in the system. This is generally accomplished with

prism or grating pairs and has been used successfully in such areas as pulse duration minimization in Ti:Sapphire laser cavities [37], dispersive measurements in microscope objectives [33,38] and ultrafast pump-probe studies [16,17]. While prism or grating pairs can be successfully used to nullify GVD effects they are not without drawbacks. In the case of two independent beam paths containing different sources of dispersion, such as in a pump-probe experiment, GVD compensation must be independently done on each beam path. As well, for sub-15 fs pulses, where 3rd and higher order effects become important, additional compensation must be introduced via highly specialized and expensive dielectric mirrors [33]. Even if implementation of the above compensation techniques is feasible, spherical and chromatic aberrations have still not been addressed.

The simplest alternative is to utilise only reflective optics and include the minimum of dispersive optical elements in the beam path. In terms of focusing elements, parabolic mirrors are well suited to ultrafast optical systems as they induce no spherical or chromatic aberration. Thus, through prudent selection of optical components and careful consideration of the geometrical factors involved in an experimental set-up, sub-25 fs temporal resolution can be readily achieved.

2.5 References

- [1] C. V. Shank and E. P. Ippen, "Anisotropic absorption saturation with picosecond pulses," *Appl. Phys. Lett.* **26**, 62 (1975).
- [2] Arthur L. Smirl, Thomas F. Boguess, B. S. Wherrett, G. Paul Perryman, and Alan Miller, "Picosecond Optically Induced Anisotropic State Filling in Semiconductors," *Phys. Rev. Lett.* **49**, 933 (1982).
- [3] J. M. Weisenfield and A. J. Taylor, "Picosecond band filling in highly excited In-Ga-As-P films," *Phys. Rev. B* **34**, 8740 (1986).
- [4] Wei-Zhu Lin, Robert W. Schoenlein, James G. Fujimoto, and E. P. Ippen, "Femtosecond Absorption Saturation Studies of Hot Carriers in GaAs and AlGaAs," *IEEE J. Quantum Electron.* **24**, 267 (1988).
- [5] G. C. Cho, W. Kütt, and H. Kurz, "Subpicosecond Time-Resolved Coherent-Phonon Oscillations in GaAs," *Phys. Rev. Lett.* **65**, 764 (1990).
- [6] Takayuki Tanaka, Akira Harata, and Tsuguo Sawada, "Subpicosecond surface-restricted carrier and thermal dynamics by transient reflectivity measurements," *J. Appl. Phys. Lett.* **82**, 4033 (1997).
- [7] Jacques I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Englewood Cliffs, New Jersey (1971).
- [8] A. Leitenstorfer, S. Hunsche, J. Shah, M. C. Nuss, and W. H. Knox, "Femtosecond Charge Transport in Polar Semiconductors," *Phys. Rev. Lett.* **82**, 5140 (1999).
- [9] Neil W. Ashcroft and N. David Mermin, *Solid State Physics*, Harcourt Brace & Company, Orlando, Florida (1976).

- [10] S. Gupta, M. Y. Frankel, J. A. Valdmanis, J. F. Whitaker, G. A. Mourou, F. W. Smith, and A. R. Calawa, "Subpicosecond carrier lifetime in GaAs grown by molecular beam epitaxy at low temperatures," *Appl. Phys. Lett.* **59**, 3276 (1991).
- [11] Nasser Peyghambarian, Stephan W. Koch, and Andre Mysyrowicz, *Introduction to Semiconductor Optics*, Prentice-Hall, Englewood Cliffs, New Jersey (1993).
- [12] F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, New York (1965).
- [13] Xing Zhou, "Ensemble Monte Carlo Modeling of High-Field Transport and Ultrafast Phenomena in Compound Semiconductors," PhD thesis, Department of Electrical Engineering, University of Rochester (June 1990).
- [14] G. K. Woodgate, *Elementary Atomic Structure*, Second Edition, Oxford University Press, New York (1992).
- [15] T. S. Moss, G. J. Burrell, and B. Ellis, *Semiconductor Opto-Electronics*, Butterworth & Co, London (1973).
- [16] P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, "Femtosecond Photon Echoes from Band-to-Band Transitions in GaAs," *Phys. Rev. Lett.* **61**, 1647 (1988).
- [17] M. T. Portella, J.-Y. Bigot, R. W. Schoenlein, J.E. Cunningham, and C. V. Shank, "*k*-space carrier dynamics in GaAs," *Appl. Phys. Lett.* **60**, 2123 (1992).
- [18] Arthur L. Smirl, "Chapter 7: Dynamics of High-Density Transient Electron-Hole Plasmas in Germanium," in *Semiconductors Probed by Ultrafast Laser Spectroscopy: Volume I*, edited by R. R. Alfano, Harcourt Brace Jovanovich, New York (1984).

- [19] B. B. Hu, E. A. de Souza, W. H. Knox, J. E. Cunningham, M. C. Nuss, A. V. Kuznetsov, and A. L. Chuang, "Identifying the Distinct Phases of Carrier Transport with 10 fs Resolution," *Phys. Rev. Lett.* **74**, 1689 (1995).
- [20] A. V. Kuznetsov and C. J. Stanton, "Ultrafast optical generation of carriers in a dc electric field: Transient localization and photocurrent," *Phys. Rev. B* **48**, 10 828 (1993).
- [21] P. A. Maksym and C. J. Hearn, "Chapter 3: Ultrafast Relaxation Processes of Hot Photoexcited Carriers," in *Semiconductors Probed by Ultrafast Laser Spectroscopy: Volume I*, edited by R. R. Alfano, Harcourt Brace Jovanovich, New York (1984).
- [22] R. Brunetti and C. Jacoboni, "Chapter 12: Transient and Stationary Properties of Hot-Carrier Diffusivity in Semiconductors," in *Semiconductors Probed by Ultrafast Laser Spectroscopy: Volume I*, edited by R. R. Alfano, Harcourt Brace Jovanovich, New York (1984).
- [23] M. A. Osman and D. K. Ferry, "Monte Carlo investigation of the electron-hole-interaction effects on the ultrafast relaxation of photoexcited carriers in GaAs," *Phys. Rev. B* **36**, 6018 (1987).
- [24] Fausto Rossi and Tilmann Kuhn, "Theory of ultrafast phenomena in photoexcited semiconductors," *Rev. Mod. Phys.* **74**, 895 (2002).
- [25] U. Hohenester, P. Supancic, P. Kocevar, X. Q. Zhou, W. Kütt and H. Kurz, "Subpicosecond thermalization and relaxation of highly photoexcited electron and holes in intrinsic and *p*-type GaAs and InP," *Phys Rev. B* **47**, 13 233 (1993).

- [26] C. L. Tang, F. W. Wise, and I. A. Wamsley, "Femtosecond Relaxation Dynamics of Nonequilibrium Carriers in GaAs and Related Compounds," *Solid-State Commun.* **31**, 439 (1988).
- [27] M. J. Kann, A. M. Kriman, and D. K. Ferry, "Effect of electron-electron scattering on intervalley transition rates of photoexcited carriers in GaAs," *Phys. Rev. B* **41**, 12 659 (1990).
- [28] P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, J. Shah, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, "Femtosecond intervalley scattering in GaAs," *Appl. Phys. Lett.* **53**, 2089 (1988).
- [29] E. P. Ippen, Lecture notes from:
<http://www.nkt.dk/summer/presen/Ippenlectures.pdf>
- [30] Z. Vardeny and J. Tauc, "Picosecond Coherence Coupling in the Pump and Probe Technique," *Opt. Comm.* **39**, 396 (1981).
- [31] Yu. P. Svirko and N. I. Zheludev, "Chapter 2: Constitutive Equations in Nonlinear Optics," in *Polarization of Light in Nonlinear Optics*, John Wiley & Sons, Toronto (1998).
- [32] M. Joffe, "Chapter 9: Coherent Effects in Femtosecond Spectroscopy: A Simple Picture Using the Bloch Equation," in *Femtosecond Laser Pulses: Principles and Experiments*, edited by C. Rullière, Springer-Verlag, New York (1999).
- [33] J. Jasapara and W. Rudolph, "Characterization of sub-10-fs pulse focusing with high-numerical-aperture microscope objectives," *Opt. Lett.*, **24**, 777 (1999).
- [34] Z. Bor, "Distortion of femtosecond laser pulses in lenses," *Opt. Lett.*, **14**, 119 (1989).

- [35] M. Kempe and W. Rudolph, "Femtosecond pulses in the focal region of lenses," *Phys. Rev. A* **48**, 4721 (1993).
- [36] Guillermo O. Mattei and Mirta A. Gil, "Spherical aberration in spatial and temporal transforming lenses of femtosecond laser pulses," *Appl. Opt.* **38**, 1058 (1999).
- [37] Chung-Po Huang, Henry C. Kapteyn, John. W. McIntosh, and Margaret M. Murnane, "Generation of transform-limited 32-fs pulses from a self-mode-locked Ti:sapphire laser," *Opt. Lett.* **17**, 139 (1992).
- [38] A. C. Millard, D. N. Fittinghoff, J. A. Squier, M. Müller and A. L. Gaeta, "Using GaAsP photodiodes to characterize ultrashort pulses under high numerical aperture focusing in microscopy," *J. Microsc.* **193**, 179 (1999).

Chapter 3

Plasmons and Phonons in Semiconductors

3.0 Introduction

The aim of this chapter is to provide the background information necessary for an understanding of coherent oscillations observed in many semiconductors following illumination on sub-picosecond timescales. First, the basic principles that govern lattice oscillation and the concept of coherent phonons is introduced. This is followed by a detailed treatment of charge density oscillations, known as plasmons, their coupling to coherent phonons and a common means by which these modes are excited, by displacive excitation. Effects resulting from high photo-injected charge carrier densities are next discussed, including the topics of anharmonic oscillations, mode softening and lattice instability. The chapter then concludes with the means by which the above material behaviours appear in time-resolved pump-probe reflectivity measurements.

3.1 An Introduction to Phonons

As previously mentioned in Chapter 2 the periodic nature of a crystalline solid plays a crucial role in the electronic physics of the medium. This periodicity also has implications with regard to the vibrational dynamics of the lattice ions, hence, thermal properties of semiconductors. In the presence of large densities of charge carriers and/or large electric fields these lattice oscillations, when excited on a sub-picosecond timescales, may exhibit coherent behaviour [1-5]. Through analysis of these coherent

lattice dynamics a wide range of fundamental semiconductor physics may be understood, in particular, ultrafast laser induced lattice instabilities and phase transitions [6-10]. Before these complex processes can be studied, the basic nature of lattice vibrations must first be understood.

Under the application of a perturbative force, such as a weak electric field, an atom in a crystal lattice will begin to oscillate about its specific lattice site, however, the motion of the atom will not be independent of its neighbouring atoms. In a first approximation the interacting atoms can be treated as a 1-D linear chain, with the interatomic forces modeled as springs connecting the nearest neighbour atoms (Figure 3.1.1). In crystals with a zincblende structure the linear chain is diatomic with alternating atoms of mass, M and m . Mathematical treatment of this simple system leads to the classical harmonic oscillator equation, with two normal mode solutions satisfying a dispersion relation between the frequency of the mode, ω , and the wave vector, $\mathbf{q}$. In Figure 3.1.2 a physical picture of the vibrational modes along with the dispersion relations are shown. The lowest order mode occurs when the two nearest neighbour atoms oscillate in phase, and results in a longitudinal mode propagating at the material speed of sound, similar in form to a pressure wave. Thus, this is known as the longitudinal acoustic (LA) mode and has a linear dispersion relation in the long wavelength (low $\mathbf{q}$) limit. The other normal vibrational mode occurs when the two nearest neighbours oscillate out of phase, maintaining the position of the centre of mass, as illustrated in Figure 3.1.2b. It is known as the longitudinal optic (LO) mode and has a nearly flat dispersion relation in the long wavelength (low $\mathbf{q}$) limit.

The number of normal oscillatory modes that are supported in a crystal depends on

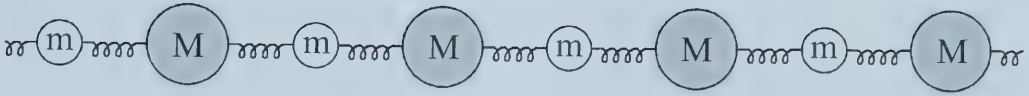


Figure 3.1.1. A 1-D linear diatomic chain of atoms of different masses M and m . The springs represent the nearest neighbour interaction forces between lattice ions.

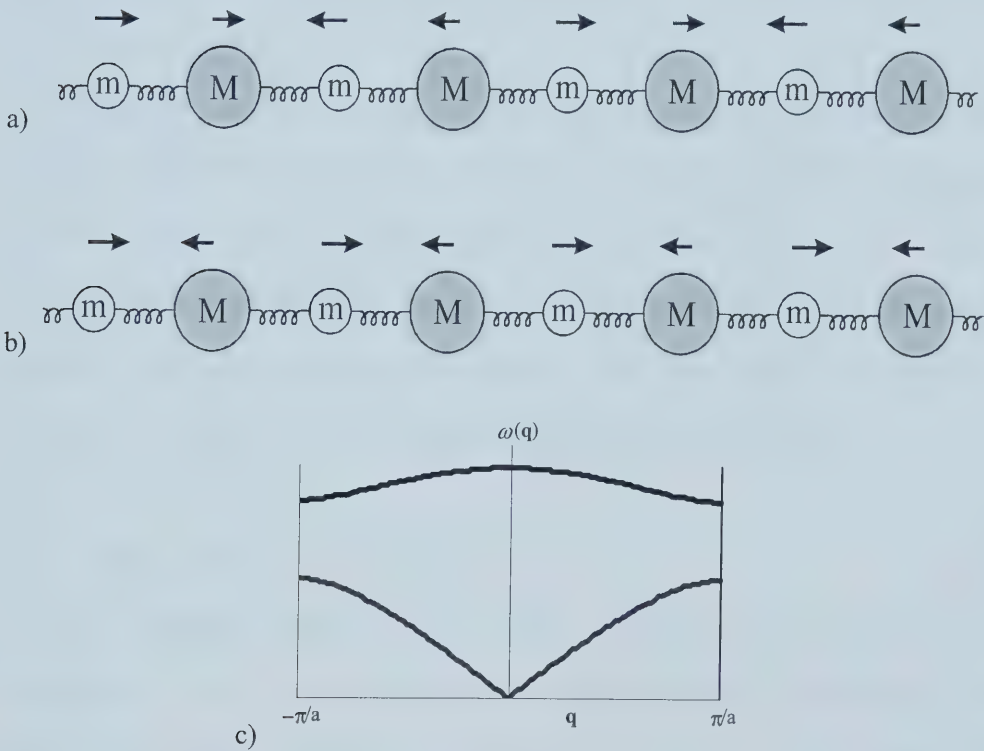


Figure 3.1.2. a) Motion of a 1-D diatomic chain of atoms in the acoustic mode. b) Optic mode for the diatomic chain. c) A typical dispersion relation for a 1-D diatomic system of atoms, where $\mathbf{q}$ is the wave vector of the mode and $\omega(\mathbf{q})$ is the oscillation frequency. The upper branch corresponds to the optic mode while the lower branch is the acoustic mode.

the number of atoms, s , that make up the unit cell of the lattice. Treatment of the crystal as a three dimensional system leads to three possible acoustic modes (one longitudinal and two transverse polarizations) and $3(s-1)$ optical modes ($(s-1)$ longitudinal and $2(s-1)$ transverse polarizations) being supported by the lattice. For the case of two atoms per unit cell, such as in a zincblende material, this implies that there are 3 acoustic and 3 optic modes. An example of the dispersion curves for a zincblende material, InSb, is shown in Figure 3.1.3, with the dispersion relations plotted in terms of the high symmetry points of the crystal.

The quantum mechanical picture of lattice vibrations does little to alter the above discussion. Only the energy of a mode is altered, as the energy of a lattice oscillation may only take on discrete values, rather than the continuous values allowed in the classical 1-D atomic chain treatment. Thus, the lattice oscillations are often treated as quantized packets of vibrational energy called phonons. This has important implications in discussion of interactions with other particles, such as electrons and holes.

3.1.1 Coherent Phonons

Under equilibrium conditions and at room temperature several different phonons modes will be present in a typical crystalline solid, due purely to the thermal energy available to the lattice. In this situation the phonons pertaining to a specific mode will not have a well-defined phase relation- they are incoherent. However, the excitation of a lattice vibrational mode on a timescale significantly less than the period of a particular phonon mode can result in a constant phase relation between a vast majority of phonons within that mode. For optical phonon modes in III-V semiconductors, with frequencies

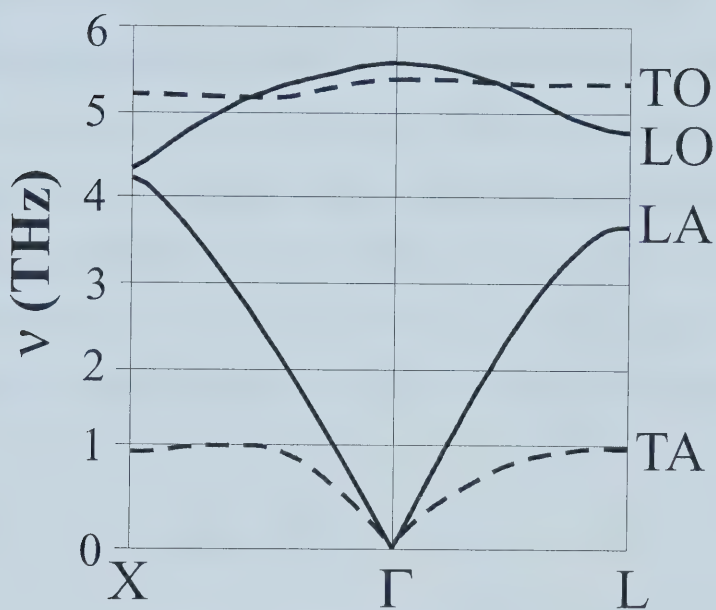


Figure 3.1.3. Dispersion curves for acoustic and optic phonons in InSb at $T = 300$ K, where Γ , L, and X are the usual high symmetry crystal directions [as calculated by reference 11]. The transverse acoustic (TA) longitudinal acoustic (LA), transverse optic (TO) and longitudinal optic (LO) phonon modes are indicated.

typically the 5-10 THz range (ex. $\nu_{LO}(\Gamma) = 8.76$ THz for GaAs), this implies the excitation must occur on a sub-50 fs timescale. The minimum excitation times required for near Brillouin-zone (BZ) centre (small $\mathbf{q}$) acoustic phonons may be much larger, as the corresponding oscillation period is sub-THz, thus, picosecond excitation may induce coherent acoustic lattice vibration [9]. For BZ-edge (large $\mathbf{q}$) acoustic phonons, due to the shape of the dispersion curve, the vibrational frequencies are similar to the optical phonon frequencies. Hence, the excitation timescales necessary for the generation of coherent zone-edge acoustic phonons are similar to those for optical phonons.

While the generation mechanism for the various modes can be quite different, the equations governing phonon motion are common. In the regime where the motion of an atom about its lattice point may be considered as harmonic the coherent-phonon displacement, $\mathbf{Q}(t)$, can be derived from a driven-damped harmonic oscillator equation [12]:

$$\ddot{\mathbf{Q}}(t) + 2\gamma_{ph}\dot{\mathbf{Q}}(t) + \omega_{ph}^2\mathbf{Q}(t) = \frac{\mathbf{F}(t)}{\mu^*}, \quad (3.1.1)$$

where: γ_{ph} is the phonon damping constant, ω_{ph} is the frequency of the coherent phonon, μ^* is the reduced mass of the unit cell and $\mathbf{F}(t)$ is the driving force on the phonon. The phonon damping constant is given by the dephasing time for the mode, $\gamma_{ph} = 1/T_2$. This dephasing time has two contributions, those due to pure phase destroying mechanisms, occurring on timescales T_I , and those due to phonon population reduction mechanisms, occurring on timescales T_p . Processes which reduce a specific phonon population include emission/absorption of a phonon by a charge carrier and phonon decay due to anharmonic processes (ex. $LO(\Gamma) \rightarrow TA(L) + LO(L)$ [13, 14]).

Equation 3.1.1 can be used to describe both acoustic and optical phonons as long as the correct identification of the displacement vector, $\mathbf{Q}(t)$, is made. In the case of the acoustic mode, all of the atoms in the unit cell move together in phase, thus, the displacement vector corresponds to the real displacement of the centre of mass of the unit cell. Contrary to this, for optic modes the centre of mass is immobile. In this instance the displacement vector describes the relative displacement between the atoms of a unit cell. For example, in a III-V semiconductor if $\mathbf{u}(t)$ corresponds to the displacement of the group III atom and $\mathbf{v}(t)$ is the displacement of the group V element then the relative displacement is given by, $\mathbf{Q}(t) = \mathbf{u}(t) - \mathbf{v}(t)$. Thus, the coherent optical phonon is described by the motion of the group III and V elements relative to each other.

A general solution for equation 3.1.1 can be written in terms of the driving force, under the assumption that the system is in equilibrium long before the application of a driving force ($\mathbf{Q}(t \rightarrow -\infty) = [\partial \mathbf{Q}(t)/\partial t]_{t \rightarrow -\infty} = 0$) [14]:

$$\mathbf{Q}(t) = \int_{-\infty}^t \frac{F(\tau)}{\mu^*} \frac{e^{-\gamma_{ph}(t-\tau)} \sin \left[\left(\omega_{ph}^2 - \gamma_{ph}^2 \right)^{\frac{1}{2}} (t-\tau) \right]}{\sqrt{\omega_{ph}^2 - \gamma_{ph}^2}} d\tau. \quad (3.1.2)$$

This relatively simple equation can be utilised to determine the behaviour of a phonon system under the application of two special classes of forces, impulsive and dispersive.

For an impulsive driving force:

$$\mathbf{F}(t) = \mathbf{I} \delta(t), \quad (3.1.3)$$

where: $\mathbf{I} = \int \mathbf{F}(t) dt$ is the total impulse delivered to the oscillating element, the solution to equation 3.1.2 takes on the form:

$$\mathbf{Q}(t) = \frac{\mathbf{I} \theta(t)}{\mu^* \sqrt{\omega_{ph}^2 - \gamma_{ph}^2}} e^{-\gamma_{ph} t} \sin \left[\left(\omega_{ph}^2 - \gamma_{ph}^2 \right)^{\frac{1}{2}} t \right]. \quad (3.1.4)$$

The impulsive excitation imparts an initial velocity to the lattice ion but the oscillation starts from its equilibrium position, $\mathbf{Q}(t \rightarrow -\infty) = 0$. Thus, the lattice atom returns to its equilibrium position for times much greater than the decay time, $T_2 = 1/\gamma_{ph}$. A plot of this behaviour is displayed in Figure 3.1.4.

A displacive driving force:

$$\mathbf{F}(t) = \mathbf{F}_0 \theta(t), \quad (3.1.5)$$

where: $\mathbf{F}_0$ is the amplitude of the forcing function, results in a slightly more complex solution for the phonon amplitude:

$$\mathbf{Q}(t) = \frac{\mathbf{F}_0 \theta(t)}{\mu^* \omega_{ph}^2} \left\{ 1 - \left[\frac{\gamma_{ph}}{\sqrt{\omega_{ph}^2 - \gamma_{ph}^2}} \sin \left(\left\{ \omega_{ph}^2 - \gamma_{ph}^2 \right\}^{\frac{1}{2}} t \right) + \cos \left(\left\{ \omega_{ph}^2 - \gamma_{ph}^2 \right\}^{\frac{1}{2}} t \right) \right] e^{-\gamma_{ph} t} \right\}. \quad (3.1.6)$$

The behaviour under a displacive force is considerably different than the impulsive case. Here, the atom is initially located at the equilibrium position, for times much before excitation, with zero initial velocity but immediately upon excitation it commences to oscillate about a new equilibrium position, analogous to the situation of a harmonic oscillator starting from its amplitude extremum with zero velocity. For times much greater than the damping time, $1/\gamma_{ph}$, the oscillator does not return to its former equilibrium position, as is seen in Figure 3.1.5.

There are several points that should be mentioned about coherent phonons before a complete description of the driving mechanisms is undertaken. A quantum mechanical calculation of the time-dependent phonon amplitude [14] places special restrictions on the wave vector of the coherent phonon mode that are not apparent in the classical calculation. In particular, a coherent phonon mode consists of a coherent superposition of

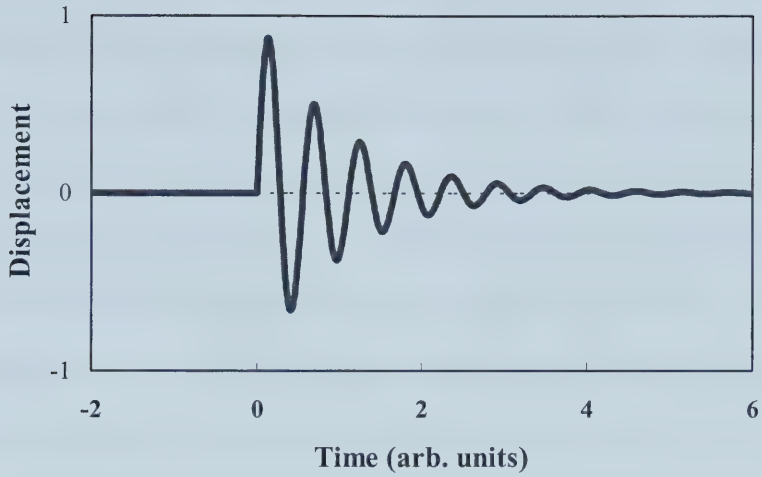


Figure 3.1.4. The displacement of a harmonic oscillator as a function of time resulting from an impulsive excitation, $\mathbf{F}(t) = \mathbf{I} \delta(t)$, in the limit of $\omega^2 \gg \gamma^2$.

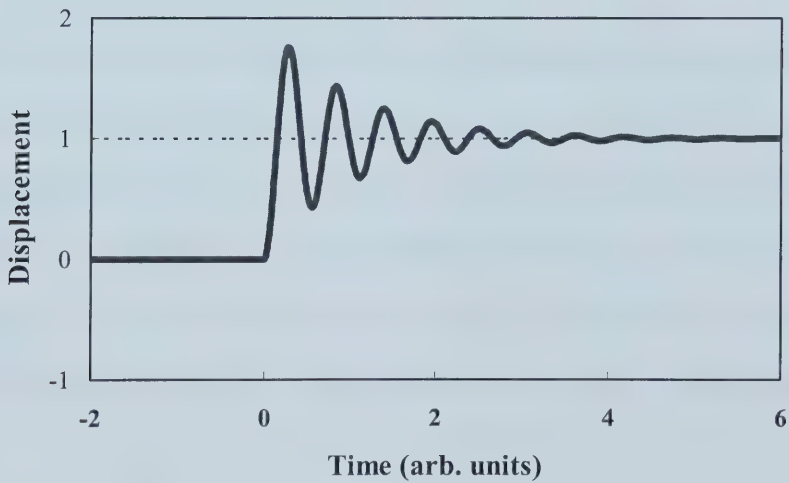


Figure 3.1.5. The displacement of a harmonic oscillator as a function of time resulting from a displacive excitation, $\mathbf{F}(t) = \mathbf{F}_0 \theta(t)$, in the limit of $\omega^2 \gg \gamma^2$. Notice that the final equilibrium position does not coincide with the initial one.

phonon states at one $\mathbf{q}$ value, not several different phase-locked modes at one frequency but different $\mathbf{q}$. This implies coherent oscillations cannot result from the phonon emission process as the carriers cool to the band edge, as the wave vector of the emitted phonon depends on the energy and momentum state of the carrier that emitted it. As the phase of a phonon emitted from one carrier has no quantum mechanical reason to be related to a phonon emitted from any other carrier (in most circumstances), phonons emitted during carrier thermalization are incoherent. Energy and momentum conservation play a crucial role in the long lifetime associated with coherent phonon modes at $\mathbf{q} = 0$. While the generation of incoherent phonons during charge thermalization can act to quickly dephase a coherent mode at $\mathbf{q} \neq 0$, energy and momentum conservation forbids incoherent phonon emission for carriers at $\mathbf{q} = 0$. As a result $\mathbf{q} = 0$ coherent phonons may only dephase through anharmonic decay, which typically takes on the order of several ps [13].

While the above information has demonstrated the general behaviour of an oscillatory mode under the influence of a driving force, it has not addressed the processes that introduce this driving force to the lattice. In semiconductors illuminated by ultrashort (femtosecond) laser pulses the coupling mechanisms between the incident light and the phonon modes are numerous and complex. Clearly, it is these coupling mechanisms which will clarify the manner in which the driving force for a given phonon mode originates.

3.2 Coupling of Longitudinal Modes to Light

One of the most common means by which coherent phonons are generated is through the interaction of an ultrashort optical pulse with the crystal. Typically, it is not the optical pulse itself which generates the coherent modes but the photo-generated charge carrier density. In the sections that follow, the relations between the photo-generated charge density and the lattice modes will be discussed in detail.

3.2.1 Plasmons

The photo-generation of electrons and holes in a semiconductor due to an ultrashort laser pulse results in a complex temporal evolution of the material, as was seen in Chapter 2. The presence of an electric field in the material, due to the voltage applied to a PC switch or a built in surface field, can further complicate the internal dynamics. Charge carriers can couple to this field leading to quantized plasma oscillations, known as plasmons. In the description that follows the generation mechanism, time evolution and coupling of plasmons to phonon modes will be discussed in detail.

Consider a free electron plasma which is at equilibrium such that the mean velocity is zero (i.e. no net field in the material). The introduction of a small charge density, N_1 , has the effect of perturbing the system equilibrium. Through the divergence of $\mathbf{E}$ in the presence of a charge density (Maxwell's first equation) and the charge continuity equation it can be shown [15] that the small perturbation in density leads to:

$$\frac{\partial^2 N_1}{\partial t^2} + \omega_{pl}^2 N_1 = 0, \quad (3.2.1)$$

where: ω_{pl} is the plasma frequency and is related to the initial charge density, N_o , of the system:

$$\omega_{pl}^2 = \frac{4\pi N_o e^2}{\epsilon m_e^*}, \quad (3.2.2)$$

where: e is the electronic charge. The solution to equation 3.2.1 is simply undamped longitudinal oscillations of the plasma at the plasma frequency.

It is evident that even in the absence of an applied field the introduction of electrons into a free electron plasma will result in plasma oscillations. In a semiconductor the situation is complicated if charge carriers are photo-excited, as equal numbers of electrons and holes are created leaving the material neutral, hence, devoid of plasmon oscillations. This can be remedied by the application of an electric field that acts to separate the charge carriers. Often, the simplifying assumption is made that the holes remain stationary, as the hole effective mass is typically much greater than the electron effective mass (ex. For GaAs, $m_e^* \approx 0.063 m_e$, $m_{hh}^* \approx 0.51 m_e$ [16]) and, therefore, the magnitude of the acceleration of an electron in the electric field would be several times greater than for a hole. In this picture, as seen in Figure 3.2.1, the electron carrier density is initially accelerated away from the hole charge density, generating a screening field, $\mathbf{E}_s(t)$, in opposition to the applied field, $\mathbf{E}_{ext}(t)$. The magnitude of the screening field can be approximated as [17]:

$$\mathbf{D}(t) = eN(t)\mathbf{x}(t), \quad (3.2.3)$$

where: $\mathbf{D}(t) = \epsilon(\omega)\mathbf{E}_s(t)$, and $\mathbf{x}(t)$ is the separation between electron and hole densities. If the charge densities are large enough so that the screening field can become greater than the applied field, before the carriers reach the boundaries of the system (electrodes in a PC switch, edge of the surface field region), the carriers reach a maximum velocity and begin to decelerate. Eventually, the screened field will become larger than the applied

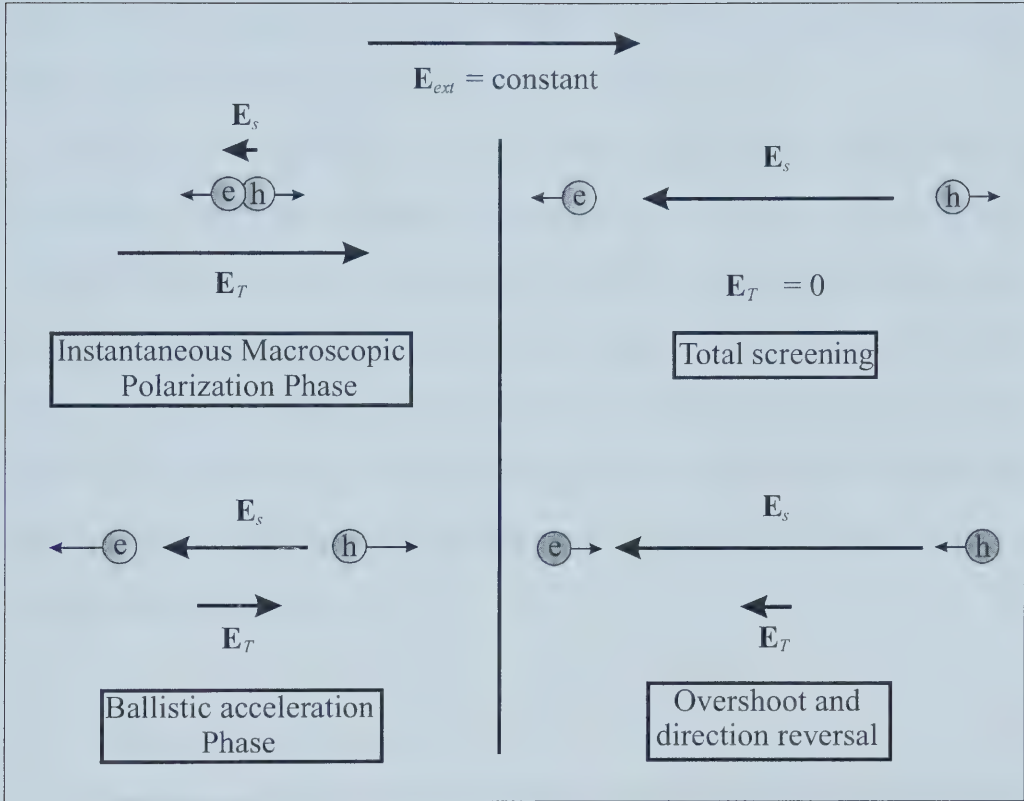


Figure 3.2.1. The initial stages of motion of photo-generated charge carriers in a constant applied field, E_{ext} . The magnitude and direction of the screening field, E_s , and total field, E_T , are show for each stage.

field, causing the carriers to reach a turning point, reverse course and accelerate towards each other. As the distance between the carriers is reduced the screened field will decrease until the screened field becomes smaller than the applied field. The carriers will then decelerate once again and reverse direction, with the end product being simple harmonic oscillation between the electron and hole distributions.

There are several different ways in which a field can be created within a semiconductor. Application of a field via an external source, such as in a PC switch [18], or built-in fields such as those observed due to Schottky contacts [19] and surface effects [1,4] are all capable of generating large fields, as high as a few hundred kV/cm [20]. While the application of large electric fields to the region of charge carrier photo-excitation has resulted in the observation of pure plasmon modes [19] often, longitudinal lattice vibrations are also seen. This behaviour can be conveniently explained through charge carrier-lattice coupling.

3.2.2 Plasmon-Phonon Coupling

The generation of plasmon oscillations through photo-excitation demonstrates that optical radiation can couple to a longitudinal mode through the creation of an electron-hole pair in an electric field. Once this longitudinal plasmon mode exists it is, therefore, possible for coupling to occur with other longitudinal modes. In many materials coupling may occur between charge carrier and longitudinal lattice oscillations to create a joint mode, known as a coupled plasmon-phonon mode. The mathematical framework for such a dynamical system is well known [12, 14] and generates some relatively simple solutions to this complex problem.

The presence of an externally applied field causes both the photo-generated carriers and the lattice to undergo collective motion. In an isotropic crystal, their equations of motion for take the form [14]:

$$\ddot{\mathbf{P}}(\mathbf{r}, t) + \gamma_{el} \dot{\mathbf{P}}(\mathbf{r}, t) + \omega_{pl}^2 \mathbf{P}(\mathbf{r}, t) = \frac{N(\mathbf{r}, t) e^2}{\epsilon_\infty \mu^*} [\mathbf{E}_{ext}(\mathbf{r}, t) - 4\pi\gamma_{12} \mathbf{Q}(\mathbf{r}, t)], \quad (3.2.4)$$

$$\ddot{\mathbf{Q}}(\mathbf{r}, t) + \gamma_{ph} \dot{\mathbf{Q}}(\mathbf{r}, t) + \omega_L^2 \mathbf{Q}(\mathbf{r}, t) = \frac{\gamma_{12}}{\epsilon_\infty} [\mathbf{E}_{ext}(\mathbf{r}, t) - 4\pi \mathbf{P}(\mathbf{r}, t)], \quad (3.2.5)$$

where: $\mathbf{P}(\mathbf{r}, t)$ is the polarization due to the separation of the electron-hole pair in the applied field, $\mathbf{E}_{ext}(\mathbf{r}, t)$, γ_{el} is the damping constant for the charge carriers, ω_{pl} is the plasma frequency as calculated from the average carrier (electron and hole) effective mass, ω_L is the longitudinal optic phonon frequency, ϵ_∞ is the high frequency dielectric function, and γ_{12} is a parameter which characterizes the strength of the carrier-lattice coupling. The coupling of phonons to the electric field is related to the transverse phonon frequency:

$$\gamma_{12} = \omega_T \sqrt{\frac{\epsilon_{DC} - \epsilon_\infty}{4\pi}}, \quad (3.2.6)$$

where: ϵ_{DC} is the low frequency dielectric constant.

A general solution to equations 3.2.4 and 3.2.5 does not exist, however, two broad observations can be:

- 1) The spatial, $\mathbf{r}$, dependence of the fields and charge densities might be expected to affect the allowed wave vectors for the modes of the system. Under the assumption of a spatially homogeneous carrier density and external field (i.e. $N(\mathbf{r}, t) \rightarrow N(t)$, $\mathbf{E}_{ext}(\mathbf{r}, t) \rightarrow \mathbf{E}_{ext}(t)$) the modes of the system would have no wave vector dependence ($\mathbf{q} = 0$).

In fact, this constraint can be further relaxed. Even if the driving forces (external field

and carrier density) are inhomogeneous, such as for tightly focused optical excitation beam spot ($\sim 1\text{-}2\ \mu\text{m}$ diameter) or the short depth in which surface/depletion fields exist ($\sim 100\ \text{nm}$ [14, 19]), typically $\mathbf{q} \sim 0$ as large wave vector modes may only be generated if the spatial variation is on the order of the lattice spacing ($a = 6.479\ \text{\AA}$ in InSb, $a = 5.65\ \text{\AA}$ in GaAs [16]). Further simplifying the analysis is the dispersion-less character of optic phonons and plasmons near $\mathbf{q} = 0$. Thus, the wave vector dependence of the excited modes can often be ignored.

- 2) There are two relaxation constants that affect the coupled system, γ_{el} and γ_{ph} . The electronic polarization dephases through momentum relaxation processes [14, 19] while the coherent phonon motion degrades as a result of anharmonic decay (for all $\mathbf{q}$) or interaction with incoherent phonons ($\mathbf{q} \neq 0$ only). Momentum dephasing times for high number densities of carriers may be as brief as tens of femtoseconds, while the dephasing of phonons can take several picoseconds [1, 13]. As a result of the coupling the lifetime of the plasmon-phonon mode would be expected to fall between the pure plasmon decay time and the lifetime of a pure phonon mode [4].

Under the assumption that the external field is constant in time a solution for equations 3.2.4 and 3.2.5, for times much before charge carrier photo-generation, can be found:

$$\mathbf{P}(t \rightarrow -\infty) = 0, \quad (3.2.7a)$$

$$\mathbf{Q}_o = \mathbf{Q}(t \rightarrow -\infty) = \frac{\gamma_{12}}{\epsilon_{\infty} \omega_L^2} \mathbf{E}_{ext}. \quad (3.2.7b)$$

As well, the steady state solution for times long after the carriers have been generated (but before recombination) may be determined:

$$\mathbf{P}(t \rightarrow +\infty) = \frac{\mathbf{E}_{ext}}{4\pi}, \quad (3.2.8a)$$

$$\mathbf{Q}(t \rightarrow +\infty) = 0. \quad (3.2.8b)$$

Clearly, the above solutions illustrate that the system moves from one equilibrium position, for times well before photo-excitation, to another, at times much after excitation. This behaviour is similar to that seen under the condition of a displacive force, where the system oscillates about and damps to a new displaced position relative to its initial equilibrium position.

The main difficulty in obtaining a simple solution of the coupled plasmon-phonon equations lies in the time-dependent number density, as it not only appears on the right hand side of equation 3.2.4 but in the plasma frequency on the left side as well. In the low carrier density, weak dephasing limit an approximate solution can be found by solving the carrier polarization equation (3.2.4) first then substituting this into the lattice ion displacement equation (3.2.5). In this limit [14]:

$$\mathbf{P}(t) = \frac{\omega_{pl}^2 \mathbf{E}_{ext}}{4\pi} [1 - I(\omega_{pl}) \cos(\omega_{pl} t)] \theta(t), \quad (3.2.9a)$$

$$\mathbf{Q}(t) = \mathbf{Q}_o \frac{I(\omega_L) \omega_{pl}^2 \cos(\omega_L t) - I(\omega_{pl}) \omega_L^2 \cos(\omega_{pl} t)}{\omega_L^2 - \omega_{pl}^2}; \quad t > 0, \quad (3.2.9b)$$

$$= \mathbf{Q}_o; \quad t < 0,$$

where: $I(\omega)$ is the ultrashort excitation pulse intensity (which generates the time dependent charge carrier density) at the given frequency, ω .

While the conditions placed upon these solutions are rather restrictive, several qualitative features of the coupled modes remain unchanged by stronger coupling conditions. A clear oscillatory character is apparent, with the system oscillating at a combination of both the plasma and longitudinal phonon frequency. This general feature

is not altered by the inclusion of stronger coupling condition. In addition, the dispersive nature of the excitation is a characteristic of plasmon-phonon coupling. Thus, the photo-generation of charge carriers in a semiconductor can result in a dispersive excitation of coherent phonons (DECP). This will be discussed in more detail in section 3.3.

For stronger coupling conditions the plasmon-phonon mode is expected to oscillate at a frequency characteristic of the joint mode. For optic modes in the homogeneous density, negligible damping limit this frequency, ω_c , can be calculated to be [12]:

$$\omega_c^\pm = \frac{1}{2} \left[\omega_{LO}^2 + \omega_{pl}^2 \pm \sqrt{(\omega_{pl}^2 + \omega_{LO}^2)^2 - 4\omega_{pl}^2\omega_{TO}^2} \right]^{\frac{1}{2}}, \quad (3.2.10)$$

where: ω_{LO} is the LO-phonon frequency and ω_{TO} is the TO-phonon frequency, arising through the coupling constant, γ_{12} . The number density dependence of the plasmon-phonon mode frequencies in GaAs is plotted in Figure 3.2.2 and shows for a given number density there are two possible modes, the lower branch, L_- , and upper branch, L_+ , at two separate frequencies. These modes display density dependent behaviour that can be divided into three regimes:

- 1) *Region I: Low Density*: In this regime the plasmon and phonon modes are not strongly coupled, as the natural plasma oscillation frequency is much less than the LO-phonon frequency. Hence, the carrier motion is unable to follow the lattice motion and the modes behave as nearly separate entities. The L_+ mode behaves almost as a pure LO-phonon mode, with a nearly carrier density independent frequency and long dephasing time (on the order of the anharmonic phonon decay time) while the L_- exhibits plasmon-like behaviour, with strong carrier density dependence and short

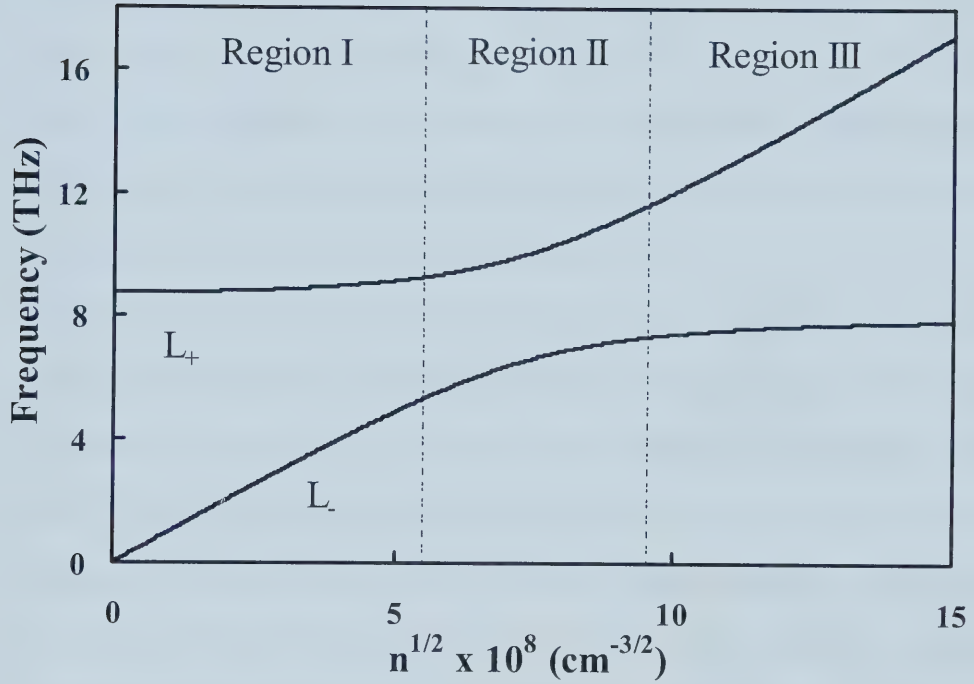


Figure 3.2.2. Upper, L_+ , and lower, L_- , branches of the coupled plasmon-phonon dispersion curve for GaAs, plotted as a function of density. The plot is divided into density three regimes: low density (Region I), anti-crossing (Region II), and high density (Region III).

dephasing time (on the order of the momentum relaxation time of the carriers).

2) *Region II: Anti-crossing*: For moderate densities both branches exhibit strong coupling, due to the near coincidence of the oscillation frequencies for both plasmon and phonon modes. The L_+ branch acquires some plasmon characteristics, exhibiting a frequency slightly greater than the natural LO-phonon frequency and a decreased lifetime, due to the increased influence of the ultrafast momentum decay of the charge carriers in the dephasing rate. In contrast, the L_- mode becomes more phonon-like with a frequency approaching the TO-phonon frequency and an increased lifetime, as a consequence of the longer phonon dephasing rate.

3) *Region III: High Density*: At high densities the plasmon and phonon modes once again become only weakly coupled, as the lattice is unable to keep up with the high frequency plasmon oscillations. The upper branch behaves as a nearly pure plasmon mode, with associated ultrafast dephasing time and density dependent oscillation frequency. The lower branch exhibits nearly pure phonon behaviour, with a slower (picosecond) decay rate and a nearly density independent oscillation frequency. Unlike the L_+ mode, which at low densities plateaus to the LO frequency, the L_- mode at high densities levels off at the TO-phonon frequency. This is a result of the partial screening of the lattice ion potential in the presence of a high charge carrier density.

In a typical transient pump-probe reflectivity experiment aimed at the observation of plasmon-phonon oscillations, at high pump powers each of these density regimes may be present within a given pump spot, as a result of the inhomogeneous spatial intensity distribution. Thus, in order to sample one particular density regime a large pump-to-probe spot diameter ratio is required. In the case where the pump and probe spot diameters are

comparable the non-uniform nature of the charge density in the region measured by the probe spot may result in the observation of two or more modes, resulting from different density regimes [14]. Interpretation of the results in this situation requires careful consideration of the experimental geometry and plasmon-phonon modes permitted, given the maximum carrier density photo-generated by the pump pulse.

3.3 Displacive Excitation of Coherent Phonons (DECP)

As discussed in section 3.1.1, the application of a displacive force to a semiconductor lattice may induce an oscillatory behaviour characterized by predominately cosine-like behaviour and harmonic motion about a new median point, relative to the initial equilibrium position. This behaviour is also apparent from the discussion in section 3.2.2, where solutions to the equations governing plasmon-phonon coupled modes exhibit motion characteristic of a displacive excitation. Often the mechanism behind the displacive excitation in time-resolved pump-probe experiments is related to charge carrier generation which, for sub-25 fs optical pulses, appears as a near step function driving force in the coupled plasmon-phonon equations of motion (3.2.4, 3.2.5). While the displacive mechanism, via ultrafast charge carrier excitation, may seem to be a common means by which coherent phonons and plasmon-phonon oscillations may be excited, other factors may contribute to prohibit the DECP mechanism.

Symmetry considerations, which may place constraints on specific material properties, can be utilised to determine the allowed dynamical behaviours of a crystal system. For coupled plasmon-phonon modes, inclusion of these symmetry considerations is normally done in the quantum mechanical model of carrier-lattice coupling (see ref.

[14]). While solution to the quantum equations of motion is beyond the scope of this dissertation the information gleaned from the calculation provides important information on the allowed generation mechanisms for the plasmon-phonon modes. In particular, for charge carrier induced DECP to be permitted an anisotropy in the carrier-crystal system must exist or symmetry considerations cause the driving force behind the oscillations to vanish. This anisotropy can be induced by the following means:

- 1) In structures of low symmetry, such as in layered materials or resulting from inherent crystallographic considerations, the pre-existing spatial non-uniformity in the crystal properties readily permits the DECP mechanism.
- 2) In cubic materials, asymmetry may be induced by the non-uniformity of the excitation process, such as due to the finite penetration depth of the excitation beam. The resultant oscillations generated in these materials are quite weak, as the inhomogeneity is quite small, resulting in a very small non-vanishing driving force.
- 3) A very efficient technique utilised to reduce crystal symmetry is the introduction of an electric field to the crystal, via external biasing, Schottky or surface fields. This creates directionality in the crystal and, therefore, allows for efficient coupling of plasmons to phonons.

Besides the system of equations governing plasmon-phonon motion and inherent symmetry considerations for DECP, the coupling between the plasmon and phonon modes needs to satisfy an additional requirement: a phonon mode may only couple to a plasmon mode of the same $\mathbf{q}$ value [14]. This result of the quantum treatment of coherent phonon excitation can be seen in the classical analogue as a result of the required phase matching condition between the two modes.

Often, DECP is said to arise from deformation potential coupling between the carriers and the lattice. In non-polar semiconductors the generation of charge carriers acts to alter the local field in the crystal. The effect on the lattice ions is to deform the potential well in which they are positioned, thereby modifying their equilibrium position and, under sufficient conditions, causing coherent oscillations to be launched. Hence, the charge carriers cause the coherent oscillations through a coupling between the lattice and the deformation potential created by the charge carriers. In polar semi-conductors, while deformation potential coupling does occur it is normally weaker than the polar (i.e. Coulomb) coupling between the charge carriers and the ionic lattice atoms [14]. Thus, in most III-V semiconductors DECP arises due to Coulombic interactions between the photo-generated charge carriers and the lattice.

3.4 Lattice Oscillations Under Large Driving Forces

The previous discussions in this chapter dealt with modes whose motion could be explained in the harmonic approximation, as the driving forces were presumed to be relatively small. For sufficiently high photo-excited carrier densities the lattice is driven such that this approximation is no longer valid and anharmonic terms must be included in the lattice equations of motion. At even higher densities, typically $\sim 10\%$ [7] of the $T = 0$ K, VB electron density ($\approx 2 \times 10^{22} \text{ cm}^{-3}$ in GaAs), certain phonon modes may become soft (i.e. frequency of the mode goes to zero) as a result of the strongly anharmonic lattice motion, indicating the crystal is undergoing a phase change into a new symmetry state. This is the regime of non-thermal melting and ultrafast phase changes, where the lattice structure is altered on a timescale significantly less than the time for energy exchange

between the hot photo-injected carriers and the lattice. In the sections that follow, the lattice behaviour in the above mentioned carrier density regimes will be discussed, beginning with the classic anharmonic oscillator.

3.4.1 The Anharmonic Oscillator

In the classical harmonic oscillator picture, in a small region about the equilibrium position the potential energy, $U(\mathbf{Q})$, of an oscillating particle can be approximated as depending on the square of the particle displacement [21]:

$$U(\mathbf{Q}) = \frac{1}{2} \mu^* \omega_o^2 \mathbf{Q}^2, \quad (3.4.1)$$

where: ω_o is the harmonic oscillator frequency. Thus, the restoring force felt by the oscillating particle depends linearly on position and appears as the term linear in $\mathbf{Q}$ in the oscillator differential equation (3.1.1). For larger amplitude motion this approximation often fails and terms of third order (and in most cases even fourth order [21]) in the displacement must be included to accurately determine the time evolution of the system. The inclusion of higher than second order terms in displacement leads to the anharmonic potential energy [21]:

$$U(\mathbf{Q}) = \frac{1}{2} \mu^* \omega_o^2 \mathbf{Q}^2 + \frac{1}{3} \mu^* a_o \mathbf{Q}^3, \quad (3.4.2)$$

where: a_o is a constant which characterizes the strength of the anharmonicity. As a result an extra term second order in the displacement appears in the left side of equation 3.1.1, creating the classical anharmonic oscillator equation:

$$\ddot{\mathbf{Q}}(t) + 2\gamma \dot{\mathbf{Q}}(t) + \omega_o^2 \mathbf{Q}(t) + a_o \mathbf{Q}^2(t) = \frac{\mathbf{F}(t)}{\mu^*}. \quad (3.4.3)$$

It can be shown [5] the frequency of oscillation for the anharmonic mode that is a solution to equation 3.4.3 obeys the simple relation:

$$\omega = \omega_o - B|\mathbf{Q}_{\max}|^2, \quad (3.4.4)$$

where: ω is the anharmonic oscillator frequency, B is a positive constant and $\mathbf{Q}_{\max}$ is the maximum displacement of the oscillator. Clearly, the effect of adding higher order terms to the potential is a reduction of the anharmonic oscillation frequency relative to the harmonic case. This mode ‘softening’ behaviour has been demonstrated in time-resolved experiments conducted on several materials in the presence of large photo-excited charge carrier densities [5, 22-24]. Mode softening is an indication that the restoring forces which act to return the lattice ions to their equilibrium positions have begun to weaken and is the first stage leading up to lattice instability. At a material-dependent (large) charge carrier density the frequency of a phonon mode may be reduced to zero, indicating that the lattice can no longer maintain its present structure and will undergo a phase transition. Such ultrafast phase transitions have been observed in time-resolved reflectivity measurement of the change in second harmonic intensity of a probe beam [6, 8, 25], indicating that the material has changed from a non-centro-symmetric structure to a centrosymmetric one.

3.4.2 Lattice Instability

The dynamics of a crystal lattice on ultrashort timescales demonstrate unusual behaviour over a wide range of excitation fluences below the material damage threshold. During the first 200-400 fs after photo-excitation the lattice in materials such as GaAs [6, 25], InSb [8, 10] and Si [26] has been observed to undergo a transition from a highly

ordered crystal structure to a considerably more disordered configuration. While the transition itself is not unusual, the rapidity of the phase change is, as it cannot be explained purely by the transfer of energy from the hot carriers to the room temperature lattice. For a carrier high above the CB minimum, carrier cooling, hence lattice heating, in III-V semiconductors is accomplished primarily by several LO-phonon emissions. A single carrier-lattice interaction will typically occur every 100-250 fs (inverse of the phonon frequency), thus, it may take from several hundred femtoseconds to several picoseconds for the charge carriers to relax to the band edge, depending on the carrier excess energy. Thus, some non-thermal process must contribute to the softening and subsequent instability of the lattice within the first few hundred femtoseconds after carrier photo-generation. A theory put forth in three publications by P. Stampfli and K. H. Bennemann [7] discusses the possible mechanisms for such ultrashort timescale structural changes in semiconductors, as summarized below.

In their first two papers, Stampfli and Bennemann discuss how the creation of a high density electron-hole plasma in a diamond or zincblende semiconductor partially destroys the attractive bonding between atoms in the crystal. This reduction in the attractive component of the bonding will cause the atoms to separate, eventually resulting in the expansion of the crystal. On ultrashort timescales the gross increase in crystal volume cannot occur as the expansion rate is limited by the sound velocity in the material. As a result, the assumption of conservation of the volume of the unit cell on ultrashort timescales is made, which implies that volume conserving shear distortions are responsible for the instability. On the femtosecond timescales involved these shear distortions result from large wave vector (from the X or L valley) TA-phonons. Stampfli

and Bennemann's theoretical calculations involving these phonon distortions indicate that for a critical charge carrier density, greater than $\sim 9\%$ of the unexcited VB electron population (N_{VB}) in silicon, the TA-phonon mode will become soft (i.e. $\omega_{TA} = 0$). At carrier densities below this value the lattice symmetry will be unaltered but the TA-phonon frequency will gradually decrease as the critical carrier density is approached. For carrier densities above the critical value the mode frequency becomes imaginary and the previously harmonic time dependence results in exponential growth of the lattice displacement in time:

$$\begin{aligned} \mathbf{Q}(t) &= \mathbf{Q}_o e^{-i\omega_{TA}t} \\ &\equiv \mathbf{Q}_o e^{\omega_{TA}t}, \end{aligned} \tag{3.4.5}$$

where : $\mathbf{Q}_o$ is the average lattice ion displacement before excitation. Further calculations in this exponential growth regime allow for a prediction of the instability onset time, determined to be the time taken for the lattice ions to be displaced 50 % of the lattice spacing. For silicon these times are calculated to be 130-330 fs for densities in the range $0.10 N_{VB} < n < 0.18 N_{VB}$ in agreement with experiments by H. W. K. Tom et al. [26].

While TA-phonon instabilities predict the behaviour of diamond structures fairly accurately it cannot explain the loss centro-symmetry observed in SH measurements in zincblende crystals. In a subsequent paper Stampfli and Bennemann propose that, in addition to the TA-phonon distortions, BZ-centre LO-phonons also contribute to the instability. Where diamond structures naturally have inversion symmetry, zincblende structures do not resulting from the two different atomic species making up the crystal lattice. For a zincblende semiconductor, the change to a new centro-symmetric structure requires that the ratio of the distance between neighbouring atomic planes must change

from 1:3 to an equal spacing configuration (See Figure 3.4.1). This can be accomplished by a long wavelength LO-phonon-like distortion, which will maintain the centre of mass of the unit cell but displace the two atomic species in opposite directions. The combination of the TA- and LO-phonon-like distortions will result in alterations to all four bonds in the tetrahedral structure of the zincblende semiconductors and will likely affect the frequency of any phonon mode within the crystal.

3.5 Reflectivity Measurement of Coherent Oscillations

The detection of coherent phonons in time-resolved reflectivity measurement is facilitated by the high degree of phase coherence of these modes and allows measurement of both the phase and amplitude of the oscillations. For most III-V semiconductors the reflectivity changes due to coherent phonons can be described via the first order Raman tensor, $\partial\chi/\partial Q$ [12]:

$$\Delta R \approx \left(\frac{\partial R}{\partial \chi_R} \right) \left(\frac{\partial \chi_R}{\partial Q} \right) \Delta Q, \quad (3.5.1)$$

where: χ_R is the real part of the optical susceptibility. The first order Raman tensor adds an orientation dependence to the reflectivity signal, thus, the amplitude of the signal will generally depend on the probe beam polarization. In many materials, due to the presence of surface or applied fields, the description of the reflectivity signal will be somewhat altered. The electric field, $\mathbf{E}$, will modify the allowed modes which can be generated as well as induce non-linear reflectivity terms. As such, the change in reflectivity due to electric field coupled phonons, such as phonon plasmon-phonon modes, becomes [27]:

$$\Delta R \approx \left[\left(\frac{\partial \chi_R}{\partial Q} \right)_E + \left(\frac{\partial \chi_R}{\partial E} \right)_Q \left(\frac{\partial E}{\partial Q} \right) \right] \Delta Q, \quad (3.5.2)$$

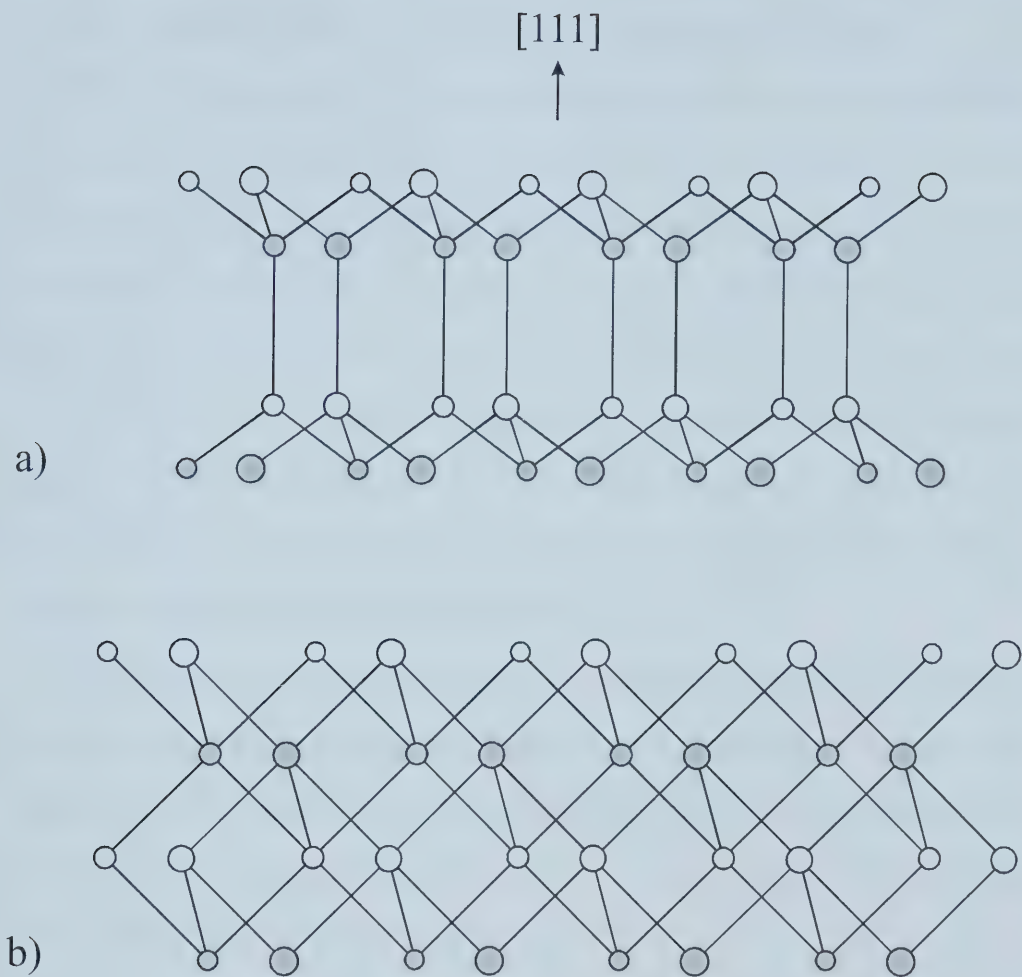


Figure 3.4.1. The effect of LO-phonon distortions on a zincblende lattice under the influence of a large charge carrier population [after reference 7]. The view is side on, with the $[111]$ direction as noted. a) Normal zincblende structure with 1:3 spacing ratio between alternate atomic planes. b) Centro-symmetric structure with a 1:1 atomic plane spacing.

where the first term corresponds to the deformation potential contribution while the second term describes electro-optic and higher order contributions to the signal.

Near the band gap energy of a semiconductor, modifications of the optical absorption in the presence of an electric field are described by the Franz-Keldysh effect [16]. For energies slightly above or below the band gap value the absorption is increased, while for energies much greater than E_g the absorption shows oscillatory behaviour as a function of energy. These induced absorption changes can be observed through changes in the electric field dependent portion of the index of refraction proportional to the third and higher odd order susceptibilities, $\chi^{(2n+1)}$ [27]. The electro-optic effect, which is proportional to $\chi^{(2)}$, is also expected to alter the index of refraction, hence, reflectivity coefficient through a term linear in the electric field

The change in the non-linear component of the index of refraction, Δn_{NL} , which is directly proportional to the change in reflectivity, can be obtained from the form of the total electric field as a function of time. The total field, $\mathbf{E}_T$, is the sum of the applied field, $\mathbf{E}_{ext}$, and the time dependent field resulting from the plasmon-phonon oscillations, $\mathbf{E}_{ph}$, with dephasing time T_2 and at frequency ω . Thus:

$$\begin{aligned}\mathbf{E}_T &= \mathbf{E}_{ext} + \mathbf{E}_{ph}, \\ &= \left[\mathbf{E}_{ext} + \mathbf{E}_o e^{-t/T_2} \cos(\omega t) \right],\end{aligned}\tag{3.5.3}$$

where: $\mathbf{E}_o$ is the maximum phonon field amplitude. The non-linear change in the index of refraction due to the electric field will be:

$$\begin{aligned}\Delta n_{NL} &\propto \chi^{(2)} \left[\mathbf{E}_{ext}(t) + \mathbf{E}_o e^{-t/T_2} \cos(\omega t) \right] + \chi^{(3)} \left[\mathbf{E}_{ext}(t) + \mathbf{E}_o e^{-t/T_2} \cos(\omega t) \right]^2 \\ &\quad + O \left\{ \chi^{(2n+1)} \left[\mathbf{E}_{ext}(t) + \mathbf{E}_o e^{-t/T_2} \cos(\omega t) \right]^{2n} \right\}.\end{aligned}\tag{3.5.4}$$

Since the applied field is typically much greater than the field accompanying the LO-phonon [27], terms of greater than linear order in $\mathbf{E}_{ph}$ may be discarded. Terms purely in the applied field, $\mathbf{E}_{ext}$, contribute to the index change only if they are time dependent and appear as the non-oscillatory component of the reflectivity signal. Thus, the index change at the plasmon-phonon oscillation frequency, $\Delta n_{NL}^{osc}(\omega, t)$, takes the form:

$$\Delta n_{NL}^{osc}(\omega, t) \propto \left\{ \chi^{(2)} + 2\chi^{(3)}\mathbf{E}_{ext}(t) + O[A_n\chi^{(2n+1)}\mathbf{E}_{ext}^{2n}(t)] \right\} \mathbf{E}_o e^{-t/\tau} \cos(\omega t), \quad (3.5.5)$$

where: A_n is a constant which depends on the order of the susceptibility, while the time dependent background changes, $\Delta n_{NL}^b(\omega, t)$, are governed by:

$$\Delta n_{NL}^b(t) = \chi^{(2)}\mathbf{E}_{ext}(t) + \chi^{(3)}\mathbf{E}_{ext}^2(t) + O[\chi^{(2n+1)}\mathbf{E}_{ext}^{2n}(t)]. \quad (3.5.6)$$

In most cubic materials the third order optical susceptibility, which dominates the Franz-Keldysh effect induced index of refraction changes in the low field regime, is nearly isotropic and, therefore, not affected by the polarization of the probe beam. For excitation near the band gap energy G.C. Cho et al. [27] have shown that the strength of the reflectivity changes proportional to $\chi^{(3)}$ are an order of magnitude larger than the linear electro-optic, $\chi^{(2)}$, contribution. Thus, the strength of the signal in most time-resolved pump-probe reflectivity experiments is determined primarily from effects linear in the third order susceptibility and is nearly independent of the probe beam polarization.

3.6 References

- [1] G. C. Cho, W. Kütt , and H. Kurz, “Subpicosecond Time-Resolved Coherent-Phonon Oscillations in GaAs,” *Phys. Rev. Lett.* **65**, 764 (1990).
- [2] T.K. Cheng, S. D. Brorson, A. S. Kazeroonian, J. S. Moodera, G. Dresselhaus, M. S. Dresselhaus, and E. P. Ippen, “Impulsive excitation of coherent phonons observed in reflection in bismuth and antimony,” *Appl. Phys. Lett.* **57**, 1004 (1990).
- [3] T.K. Cheng, J. Vidal, H. J. Zeiger, G. Dresselhaus, M. S. Dresselhaus, and E. P. Ippen, “Mechanism for displacive excitation of coherent phonons in Sb, Bi, Te, and Ti_2O_3 ,” *Appl. Phys. Lett.* **59**, 1923 (1991).
- [4] G. C. Cho, T. Dekorsy, H. J. Bakker, R. Hövel, and H. Kurz, “Generation and Relaxation of Coherent Majority Plasmons,” *Phys. Rev. Lett.* **77**, 4062 (1996).
- [5] Muneaki Hase, Masahiro Kitajima, Shin-ichi Nakashima, and Kohji Mizoguchi “Dynamics of Coherent Anharmonic Phonons in Bismuth Using High Density Photoexcitation,” *Phys. Rev. Lett.* **88**, 067401-1 (2002).
- [6] S. V. Govorkov, Th. Schröder, I. L. Shumay, and P. Heist, “Transient gratings and second-harmonic probing of the phase transformation of a GaAs surface under femtosecond laser irradiation,” *Phys. Rev. B* **46**, 6 864 (1992).
- [7] P. Stampfli and K. H. Bennemann, “Theory for the instability of the diamond structure of Si, Ge, and C induced by a dense electron-hole plasma,” *Phys. Rev. B* **42**, 7163 (1990); “Dynamical theory of the laser-induced lattice instability of silicon,” *Phys. Rev. B* **46**, 10 686 (1992); “Time dependence of the laser-induced femtosecond lattice instability of Si and GaAs: Role of longitudinal optical distortions,” *Phys. Rev. B* **49**, 7299 (1994).

- [8] I. L. Shumay and U. Höfer, “Phase transformation of an InSb surface induced by strong femtosecond laser pulses,” *Phys. Rev.* **B53**, 15 878 (1996).
- [9] A. M. Lindenberg, I. Kang, S. L. Johnson, T. Missalla, P. A. Heimann, Z. Chang, J. Larsson, P.H. Bucksbum, H. C. Kapteyn, H. A. Padmore, R. W. Lee, J. S. Wark, and R. W. Falcone, “Time-Resolved X-ray Diffraction from Coherent Phonons during a Laser-Induced Phase Transition,” *Phys. Rev. Lett.* **84**, 111 (2000).
- [10] A. Rousse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebban, G. Grillon, Ph. Balcou, E. Förster, J. P. Geindre, P. Audebert, J. C. Gauthier, and D. Hulin, “Non-thermal melting in semiconductors at femtosecond resolution,” *Nature* **410**, 65 (2001).
- [11] D. L. Price, J. M. Rowe and R. M. Nicklow, “Lattice Dynamics of Grey Tin and Indium Antimonide,” *Phys. Rev. B* **3**, 1268 (1971).
- [12] Thomas Dekorsy, Gyu Cheon Cho, and Heinrich Kurz, “Chapter 4: Coherent Phonons in Condensed Media,” in *Light Scattering in Solids VIII: C60, Semiconductor Surfaces, Coherent Phonons*, edited by M. Cardona and G. Guntherodt, Springer-Verlag, (2000).
- [13] F. Valleé and F. Bogani, “Coherent time-resolved investigation of LO-phonon dynamics in GaAs,” *Phys. Rev. B* **43**, 12 049 (1991).
- [14] Alex. V. Kuznetsov and Christopher J. Stanton, “Chapter 7: Theory of Coherent Phonon Oscillations in Bulk GaAs,” in *Ultrafast Phenomena in Semiconductors*, edited by Kong-Thon Tsen, Springer-Verlag, New York (2001).
- [15] Nasser Peyghambarian, Stephan W. Koch, and Andre Mysyrowicz, *Introduction to Semiconductor Optics*, Prentice-Hall, Englewood Cliffs, New Jersey (1993).

- [16] *Handbook Series on Semiconductor Parameters*, edited by M. Levinshtein, S. Rumyantsev, and M. Shur, World Scientific Publishing Co. Pte. Ltd., Singapore (1999).
- [17] A. Leitenstorfer, S. Hunsche, J. Shah, M. C. Nuss, and W. H. Knox, "Femtosecond high-field transport in compound semiconductors," *Phys. Rev. B* **61**, 16 642 (2000).
- [18] M. D. Cummings, J. F. Holzman, and A. Y. Elezzabi, "Femtosecond carrier dynamics in an asymmetrically excited GaAs photoconductive switch," *Appl. Phys. Lett.* **78**, 3535 (2001).
- [19] W. Fischler, P. Buchberger, R. A. Höpfel and G. Zandler, "Ultrafast reflectivity changes in photoexcited GaAs Schottky diodes," *Appl. Phys. Lett.* **68**, 2778 (1996).
- [20] T. Dekorsy, T. Pfeifer, W. Kütt, and H. Kurz, "Subpicosecond carrier transport in GaAs surface-space-charge fields," *Phys. Rev. B* **47**, 3842 (1993).
- [21] Neil W. Ashcroft and N. David Mermin, *Solid State Physics*, Harcourt Brace & Company, Orlando, Florida (1976).
- [22] M. D. Cummings and A. Y. Elezzabi, "Ultrafast impulsive excitation of coherent longitudinal acoustic phonon oscillations in highly photoexcited InSb," *Appl. Phys. Lett.* **79**, 770 (2001).
- [23] T. K. Cheng, L. H. Acioli, J. Vidal, H. J. Zeiger, G. Dresselhaus, M. S. Dresselhaus and E. P. Ippen "Modulation of semiconductor-to-semimetal transition at 7 THz via coherent lattice vibrations," *Appl. Phys. Lett.* **62**, 1901 (1993).
- [24] S. Hunsche, K. Weinecke, T. Dekorsy and H. Kurz, "Impulsive Softening of Coherent Phonons in Tellurium," *Phys. Rev. Lett.* **75**, 1815 (1995).

- [25] K. Sokolowski-Tinten, J. Bialkowski, and D. von der Linde, “Ultrafast laser-induced order-disorder transitions in semiconductors,” *Phys. Rev. B* **51**, 14 186 (1995).
- [26] H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz, “Time-Resolved Study of Laser-Induced Disorder of Si Surfaces,” *Phys. Rev. Lett.* **60**, 1438 (1988).
- [27] G. C. Cho, H. J. Bakker, T. Dekorsy, and H. Kurz, “Time-resolved observation of coherent phonons by the Franz-Keldysh effect,” *Phys. Rev. B* **53**, 6904 (1996).

Chapter 4

Time-Resolved Reflectivity Measurement in GaAs

4.0 Introduction

The principle aim of this chapter is to outline the experimental system utilised to conduct time-resolved pump-probe reflectivity measurements of the ultrashort timescale carrier and lattice dynamics in the semiconductors and photo-conductive switch discussed in this thesis. In the first section, an outline of the optical set-up and data acquisition components employed in the subsequent chapters is given. The experimental system is then applied in the measurement of the sub-picosecond reflectivity of GaAs for a range of photo-excited charge carrier densities. A model of the reflectivity signal is then developed and a discussion of its validity is undertaken.

4.1 Time-Resolved Pump-Probe Reflectivity Set-up

A representation of the experimental set-up used for all time-resolved pump-probe reflectivity measurements discussed in this thesis is illustrated in Figure 4.1.1. The optical system can be divided into three main parts: the laser oscillator, the optical set-up and the detection/data acquisition components. As shown in the figure the output from the laser source is split into an intense pump and a weaker intensity probe pulse, which are both directed onto the sample of study. The reflected probe light is collected by a detector, then amplified and analysed by a computer program. In the paragraphs which follow each of the above mentioned components will be discussed in detail.

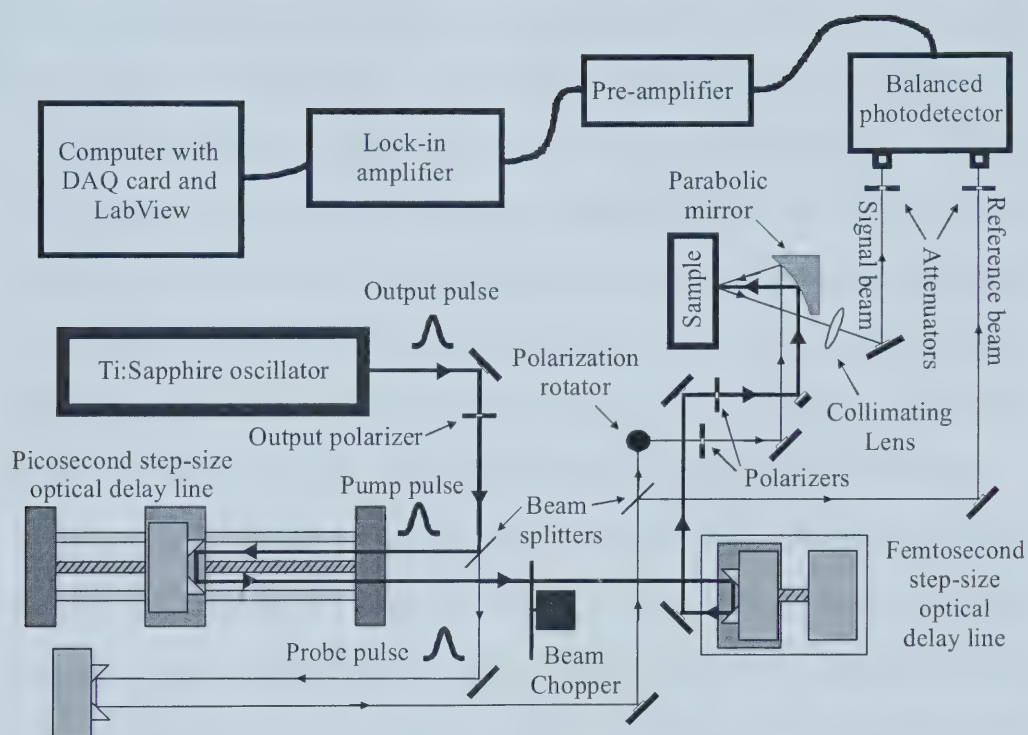


Figure 4.1.1. The experimental set-up utilised in all experiments described in this thesis. Typically, the pump beam strikes the sample at normal incidence while the probe beam is incident at a slight angle to the normal ($\theta \sim 10^\circ$).

One of two different Ti:Sapphire laser oscillators was utilised for all experiments. The first laser source (Ti:S1), a Ti:Sapphire laser oscillator, is mode-locked in order to produce output optical pulses $\tau_p = 10$ fs in duration, at a repetition rate of 80MHz with the central wavelength of the pulse spectrum centred at $\lambda_o = 810$ nm. The second Ti:Sapphire laser oscillator (Ti:S2) outputs $\tau_p = 12$ fs optical pulses at a repetition rate of 75 MHz with pulse spectrum centred about $\lambda_o = 790$ nm. The output radiation of both Ti:Sapphire lasers is highly linearly polarized and in an orientation parallel to the top surface of the optical table. In order to allow variation of the output power, a linear polarizer is placed in the beam path before the output is split into pump and probe beams. The polarizer, produced by Corning, is of sub-millimetre thickness, to reduce the effects of dispersion on the ultrashort duration optical pulses, and has a pass-band between $\lambda = 740$ -860nm.

In order to create the pump and probe pulses, the output from the Ti:Sapphire oscillator is directed onto a 1 mm thick, dielectric coated, fused-silica beam splitter. The coatings are engineered such that 20 % of the incident pulse intensity is transmitted (in the direction of the probe beam path) and 80 % of the intensity is reflected (along the pump beam path). After reflecting off the beam splitter, the pump pulse is first directed along an optical delay line, to allow variation between the pump and probe arrival times at the sample. The delay line consists of two separate stepper motor stages, each of which has a corner reflector mounted to it. The first stepper motor stage provides the coarse adjustment of the delay time, in units of 80 fs/step, while the second stepper motor stage allows for finer adjustments, in units of 0.463 fs/step. Both motors are controlled via a custom designed Labview program. An optical chopper, located between the two stepper motor stages, modulates the intensity of the pump beam at a specific frequency, typically

1.4 kHz. Upon exiting the delay line the pump beam passes through a linear polarizer and is directed, via dielectric coated or metallic mirrors, onto a gold coated 90°-off axis parabolic mirror of focal length $f = 50.8$ mm and focused onto the sample of study.

Subsequent to the transmission through the beam splitter, the probe pulse is reflected off a stationary corner reflector, which maintains an approximately equal beam path length between the pump and probe beam. The probe beam is then directed, via dielectric coated or metallic mirrors, onto another beam splitter. Half of the intensity is reflected along the path to the sample while the transmitted half (Reference beam) is directed onto a photo-detector. Using two mirrors, the reflected intensity is then polarization rotated by 90° and passed through a linear polarizer. This polarizer is oriented such that the polarization of the pump and probe beam are orthogonal. The probe beam now strikes the far side of the parabolic mirror, is focused onto the region of the sample illuminated by the pump spot and reflects off the sample surface. A lens collimates the probe light which is then collected by a photo-detector.

Reflectivity measurement is achieved through the use of a Nirvana (Model 2007) photo-detector functioning in autobalanced mode. For autobalanced detection, the light reflected from the sample (Signal) and the reference beam are focused onto the photodiodes at the front end of the Nirvana, with the reference beam intensity approximately 2 times the signal beam intensity. For optimum performance both reference and signal power must be between 0.1 mW and 1 mW at the detector. The reference and probe beam intensities are controlled by variable attenuators at the photo-detector input. Due to the intensity modulation of the pump beam, the probe beam reflected from the sample will be modulated at the optical chopper frequency. As a result,

the loop bandwidth of the Nirvana is maintained at 80, so that the autobalancing occurs on a longer timescale than the modulation of the signal.

The output voltage from the Nirvana photo-detector is amplified by a Stanford Research Systems SR560 voltage pre-amplifier before being fed into a Stanford Research Systems SR830 DSP lock-in amplifier. Significant noise reduction is provided through the lock-in amplification at the pump beam modulation frequency. Data acquisition is carried out through a custom made Labview program which controls both stepper motor stage motion and acquisition of the data from the lock-in amplifier.

4.2 Time-Resolved Pump-Probe Reflectivity Signals in GaAs

The experiment is performed at room temperature on a single $\sim 620 \mu\text{m}$ thick semi-insulating (SI)-GaAs sample (resistivity, $\rho = 5 \times 10^7 \Omega \cdot \text{cm}$) with surface normal in the [100] direction, polished to optical quality. A list of the general GaAs material parameters relevant to this study is catalogued in Table 4.1. For this experiment the laser source was Ti:S2, which outputs $\tau_p = 12$ fs pulses. Both the pump and probe beams are focused onto the sample via the same parabolic mirror, with the pump beam striking the sample at normal incidence and the probe beam striking at an incident angle of $\theta_{probe} \approx 12^\circ$. The pump and probe spots sizes are measured with the knife-edge technique. While the probe spot is essentially circular, with a diameter of $5.5 \mu\text{m}$, the pump beam is highly elliptical, with a horizontal diameter of $13 \mu\text{m}$ and a vertical diameter of $20 \mu\text{m}$. From the probe spot diameter, angle of incidence and including the dispersive effects of the pump-probe beam splitter on the probe duration, the temporal resolution is estimated to be, $\tau_{res} = 25$ fs. Adjustment of the pump and probe power is accomplished via rotation of

Table 4.1. Relevant material characteristics of SI-GaAs

Parameter	Symbol	Value
Band gap energy ($T = 300$ K)	E_g	1.424 eV [1]
Γ -valley electron effective mass	m_e^*	$0.063 m_e$ [1]
Heavy-hole effective mass	m_{hh}^*	$0.51 m_e$ [1]
Light-hole effective mass	m_{lh}^*	$0.082 m_e$ [1]
Index of refraction at 790 nm	n_c	3.68 [2]
Extinction coefficient at 790 nm	k	~ 0.083 [2]
Absorption depth at 790 nm	δ	~ 800 nm [2]

a linear polarizer placed in the source beam before it is split into pump and probe pulses. In this configuration the power is varied over an order of magnitude while the pump-to-probe power ratio is maintained at $\sim 10:1$. Differential and lock-in detection is carried out at the frequency of the optical chopper, $f_{chopper} = 1.4$ kHz. A summary of these experimental parameters is catalogued in Table 4.2.

4.3 Reflectivity Changes in GaAs

4.3.1 Sub-Picosecond Reflectivity Response

The aim of this experiment is to provide information on the sub-picosecond dynamics which result from the photo-injection of $N = 10^{18} - 10^{19} \text{ cm}^{-3}$ charge carriers into a SI-GaAs sample at room temperature. At the output photon energy of the Ti:Sapphire oscillator, $E_p = 1.55$ eV ($\lambda_o = 790$ nm), photo-excited charge carriers are generated from

Table 4.2. GaAs reflectivity experimental parameters

Parameter	Symbol	Value
Laser centre wavelength	λ_o	790 nm
Output laser pulse duration	τ_p	12 fs
Pump spot size (horizontal×vertical axes)	$a_{pump} \times b_{pump}$	$13 \times 20 \mu\text{m}^2$
Probe spot size (horizontal×vertical axes)	$a_{probe} \times b_{probe}$	$5 \times 6 \mu\text{m}^2$
Pump power range (at sample)	P_{pump}	5.7 - 56 mW
Pump-to-probe power ratio	R_{power}	10:1
Pump angle of incidence	θ_{pump}	$\sim 0^\circ$
Probe angle of incidence	θ_{probe}	$\sim 15^\circ$
Measurement resolution	τ_{res}	25 fs
Chopping frequency	$f_{chopper}$	1.4 kHz

both the heavy- and light-hole valence bands; split-off band excitation is not permitted as the laser photon energy must exceed 1.71 eV for this to occur. This results in two distributions of electrons in the CB and two distributions of holes in the VB, slightly separated in energy. As per the discussion in sections 2.2.3, the large effective mass difference between heavy- and light-holes coupled with the linear polarization of the pump beam electric field generates a carrier momentum distribution oriented primarily parallel to the probe beam polarization. Within several hundred femtoseconds the carriers are expected to interact amongst one another, randomizing energy and momentum which leads to the thermalization of the photo-carrier energy distributions. On longer timescales ranging from a few hundred femtoseconds to several picoseconds, the process of energy

relaxation occurs, whereby the carrier distributions relax to their respective band edges via the emission of incoherent phonons.

The results of the sub-picosecond time-resolved reflectivity measurement on the SI-GaAs sample in which the pump power was varied over an order of magnitude are shown in Figure 4.3.1. For each data set the general shape of the curve, hence, carrier relaxation dynamics, within 500 fs of photo-excitation are similar: near the time zero the reflectivity signal exhibits a sharp peak which is followed a more gentle rise. As the photo-generated charge carrier density is increased from, $N = 2.6 \times 10^{18} \text{ cm}^{-3}$ (for Set 12) to $N = 2.8 \times 10^{19} \text{ cm}^{-3}$ (for Set 1) the most visible change occurs for the first peak, with the magnitude increasing relative to the slower reflectivity rise and an apparent decrease in the fall time. The relatively simple nature of the reflectivity changes with carrier density suggest that, perhaps, comparatively few semiconductor interactions, such as carrier-carrier or carrier-phonon scattering, are involved in the evolution of the signals in this density regime. As such, characterization of the time-resolved reflectivity changes may enable the determination of fundamental material parameters, such as momentum dephasing and energy relaxation times.

4.3.2 Model of the Sub-Picosecond Reflectivity Dynamics in GaAs

In order to better understand the nature of the reflectivity changes pictured in Figure 4.3.1 a least squares fitting algorithm is employed to match an empirical model to the experimental data. On the sub 500-fs timescales of interest, relatively few processes may act to remove charge carriers from the region of $\mathbf{k}$ -space observed by the probe beam. As such, the aim of this study is to determine the value of the initial relaxation decay time,

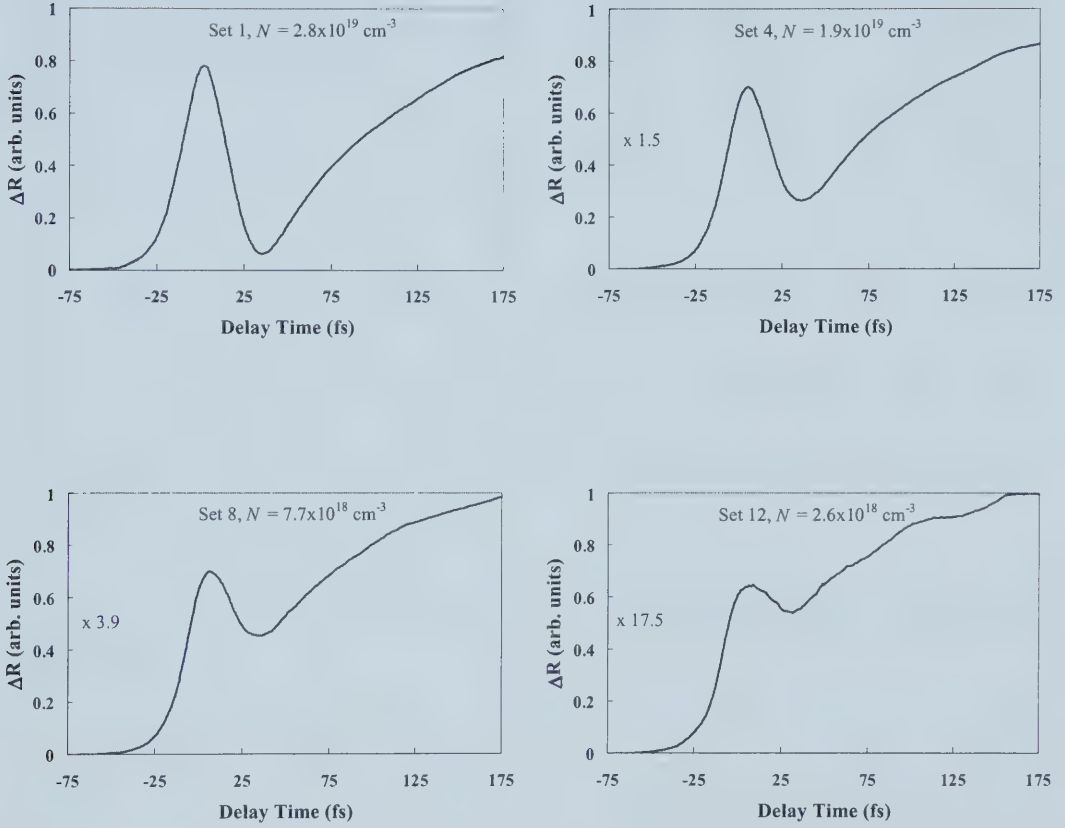


Figure 4.3.1. Reflectivity response of a SI-GaAs sample measured via time-resolved pump-probe reflectivity. The photo-excited carrier densities are indicated.

which is anticipated to be the momentum dephasing time for the charge carriers. The model is based upon the discussion in section 2.3 of Chapter 2, which states the time-resolved pump-probe reflectivity signal can be described through a third order tensor involving the polarization dependent material response, convolved with the pump and probe temporal profiles (equations 2.3.25a and 2.3.25b):

$$\gamma_{\perp}(\tau) = \int_{-\infty}^{\infty} |E_m(t-\tau)|^2 R_{xxyy}(t-t') |E_p(t')|^2 dt' dt, \quad (4.3.1a)$$

$$\beta_{\perp}(\tau) = \int_{-\infty}^{\infty} E_m^*(t-\tau) E_p(t) R_{xyyx}(t-t') E_p^*(t') E_m(t'-\tau) dt' dt, \quad (4.3.1b)$$

where: $\gamma_{\perp}(\tau)$ is the population dependent component of the signal, $\beta_{\perp}(\tau)$ is the coherent coupling term and τ is the pump-probe delay time. In this experiment the pump and probe polarizations are orthogonal.

As per the shape of the reflectivity signal the material response is formulated as two independent terms:

$$R_{ijkl}(t-t') = {}^1R_{ijkl}(t-t') + {}^2R_{ijkl}(t-t'). \quad (4.3.2)$$

The first term is responsible for the earliest timescale behaviour about the initial reflectivity peak and takes the form of a decaying exponential function:

$${}^1R_{ijkl}(t-t') = {}^1C_{ijkl} e^{-\frac{t-t'}{\tau_1}} \theta(t-t'), \quad (4.3.3)$$

where: ${}^1C_{ijkl}$ is a constant with the symmetry of the third order susceptibility tensor and τ_1 is the decay time for the first component of the material response. The second term in the material response describes the slower reflectivity rise and has the form:

$$^2R_{ijkl}(t-t') = ^2C_{ijkl} \left\{ 1 - e^{-\frac{[(t-t_2)-t']}{\tau_2}} \right\} \theta[(t-t_2)-t'], \quad (4.3.4)$$

where: $^2C_{ijkl}$ is a constant with the symmetry of the third order susceptibility tensor, t_2 is the delay between the zero time and the initiation of this term in the material response and τ_2 is the decay time. For each term the Heaviside theta function, $\theta(t)$, appears in order to impose causality, thereby limiting the response to times beyond the first interaction of the laser with the material.

In the time domain, the electric field profile of the optical pulses produced from the Ti:Sapphire oscillator utilised in all experiments can be reasonably approximated by a hyperbolic secant. Thus:

$$|\mathbf{E}_{m,p}| = |\mathbf{E}_{m,p}^o| \operatorname{sech}\left(\frac{t}{\tau_s}\right), \quad (4.3.5)$$

where: $\mathbf{E}_{m,p}^o$ is the amplitude of the probe (m) or pump (p) field and $\tau_s = \tau_p/1.762$ is the factor describing the temporal width of the hyperbolic secant field. Now, the integrations given in equations 4.3.1a and 4.3.1b may be carried out. The complex nature of the integrals, as a result of the field profiles and material response functions used in this model, necessitates the use of numerical techniques; thus, the integrals have been cast into a form that is most convenient for numerical integration. For $\beta_{\perp}(\tau)$:

$$\beta_{\perp}(\tau) = \beta_1(\tau) + \beta_{2a}(\tau) + \beta_{2b}(\tau), \quad (4.3.6)$$

where:

$$\beta_1(\tau) = C_1 \eta \int_0^1 \int_0^x \frac{\left(\frac{1}{x} - 1\right)^{\frac{\tau_s}{2\tau_1}} \left(\frac{1}{y} - 1\right)^{\frac{-\tau_s}{2\tau_1}}}{[\eta + x(1-\eta)][\eta + y(1-\eta)]} dy dx, \quad (4.3.6a)$$

$$\beta_{2a}(\tau) = C_2 \frac{\eta}{1-\eta} \int_0^1 \frac{\ln[x(1-\eta\delta) + \eta\delta] - \ln[\eta x(1-\delta) + \eta\delta]}{x(1-\eta) + \eta} dx, \quad (4.3.6b)$$

$$\beta_{2b}(\tau) = -C_2 \eta e^{\frac{t_2}{\tau_2}} \int_0^1 \int_0^{\frac{x}{x(1-\delta)+\delta}} \frac{\left(\frac{1}{x}-1\right)^{\frac{\tau_s}{2\tau_2}} \left(\frac{1}{y}-1\right)^{\frac{-\tau_s}{2\tau_2}}}{[\eta + x(1-\eta)][\eta + y(1-\eta)]} dy dx. \quad (4.3.6c)$$

For $\gamma_{\perp}(\tau)$:

$$\gamma_{\perp}(\tau) = \gamma_1(\tau) + \gamma_{2a}(\tau) + \gamma_{2b}(\tau), \quad (4.3.7)$$

where:

$$\gamma_1(\tau) = C_1 e^{\frac{-(\tau-t_o)}{\tau_1}} \int_0^1 \int_0^{\frac{x}{x(1-\eta)+\eta}} \left(\frac{1}{x}-1\right)^{\frac{\tau_2}{2\tau_1}} \left(\frac{1}{y}-1\right)^{\frac{-\tau_s}{2\tau_1}} dy dx, \quad (4.3.7a)$$

$$\gamma_{2a}(\tau) = C_2 \frac{\{\eta\delta[\ln(\eta\delta)-1]+1\}}{(\eta\delta-1)^2}, \quad (4.3.7b)$$

$$\gamma_{2b}(\tau) = -C_2 e^{\frac{-(\tau-t_o-t_2)}{\tau_2}} \int_0^1 \int_0^{\frac{x}{x(1-\eta\delta)+\eta\delta}} \left(\frac{1}{x}-1\right)^{\frac{\tau_s}{2\tau_2}} \left(\frac{1}{y}-1\right)^{\frac{-\tau_s}{2\tau_2}} dy dx, \quad (4.3.7c)$$

and:

$$\eta = e^{\frac{2(\tau-t_o)}{\tau_s}}, \quad (4.3.8a)$$

$$\delta = e^{\frac{2t_2}{\tau_s}}. \quad (4.3.8b)$$

In the above equations, t_o is defined as the pump-probe overlap time. For notational simplicity the amplitude coefficients have been re-written as: ${}^1C_{xyyx} = C_1$, ${}^2C_{xyyx} = C_2$, ${}^1C_{xxyy} = A C_1$, and ${}^2C_{xxyy} = A C_2$. With this definition the total response becomes:

$$R(\tau) = \beta_{\perp}(\tau) + A\gamma_{\perp}(\tau). \quad (4.3.9)$$

The general behaviour of the components of $\beta_{\perp}(\tau)$ is illustrated in Figure 4.3.2. Regardless of the values of the input parameters both $\beta_1(\tau)$ and $\beta_2(\tau)$ are always symmetric about t_o , hence, $\beta_{\perp}(\tau)$ is always symmetric. This is anticipated, as $\beta_{\perp}(\tau)$ is a result of the coherence between the pump and probe fields and, therefore, should have the symmetric shape of the pump-probe intensity autocorrelation function. Clearly, this term only contributes to the amplitude of the reflectivity signal in a small temporal region about the pump-probe overlap time. Contrary to this, $\gamma_{\perp}(\tau)$ describes the evolution of the population (i.e. charge carrier density), therefore, its components have a markedly different character, as illustrated in Figure 4.3.3. The shape of $\gamma_1(\tau)$ suggests it depicts the carrier generation process and a subsequent relaxation, while the $\gamma_2(\tau)$ term describes an entirely different carrier-dependent process which causes a rise in the reflectivity. Thus, $\gamma_{\perp}(\tau)$ is responsible for the shape of the reflectivity curve for all times, including and beyond the pump-probe overlap.

4.3.3 Explanation of Results

The numerical fitting of the data of Figure 4.3.1 is accomplished through a least squares fitting algorithm written in Visual C++ (see Appendix A). All numeric integration is via a Simpson's rule routine built into the least squares fitting code. Six variables are permitted to change, A , C_1 , C_2 , τ_1 , τ_2 , and t_2 , while the two remaining variables, τ_p and t_o , are fixed. The pulse width is fixed at $\tau_p = 18$ fs, which corresponds to the best fit of the initial reflectivity peak for each of the data sets, while the pump-probe overlap time, t_o , is fixed independently for each set of experimental data. Figure 4.3.4 illustrates the fit for three different values of τ_p , 16 fs, 18 fs and 20 fs. For each curve the

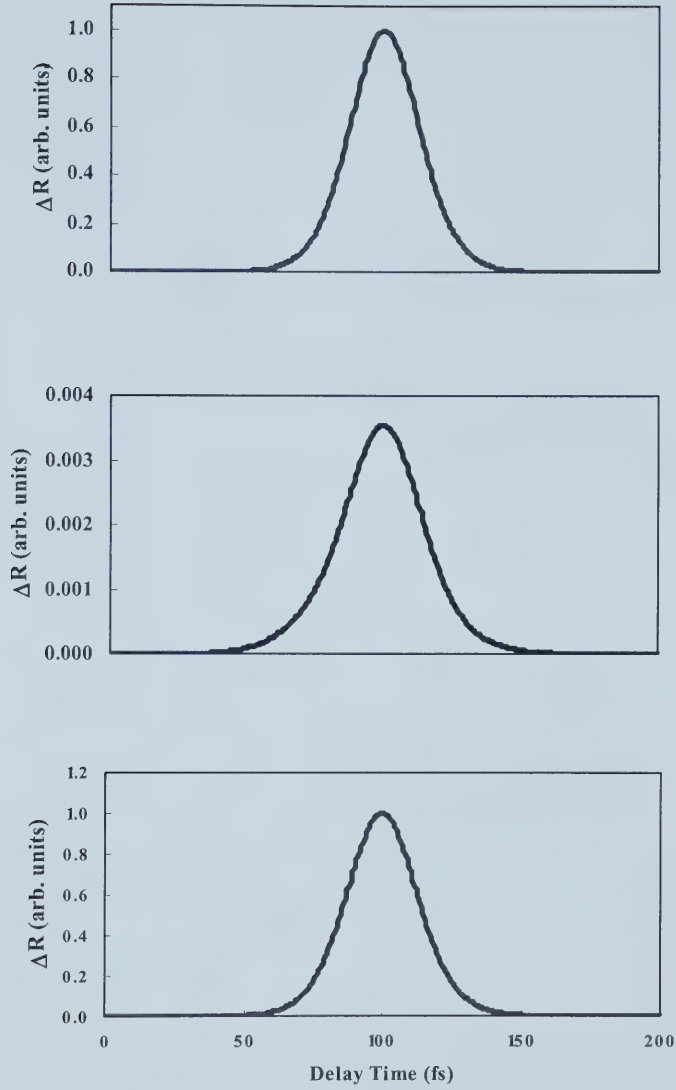


Figure 4.3.2. Plots of the two components of $\beta_{\perp}(\tau)$, for $A = C_1 = C_2 = 1.0$, $\tau_1 = 50$ fs, $\tau_2 = 80$ fs, $t_2 = 40$ fs, $t_o = 100$ fs, $\tau_p = 18$ fs. a) The $\beta_1(\tau)$ component. b) The $\beta_2(\tau) = \beta_{2a}(\tau) + \beta_{2b}(\tau)$ component. c) The sum $\beta_1(\tau) + \beta_2(\tau)$. All three plots are normalized to c).

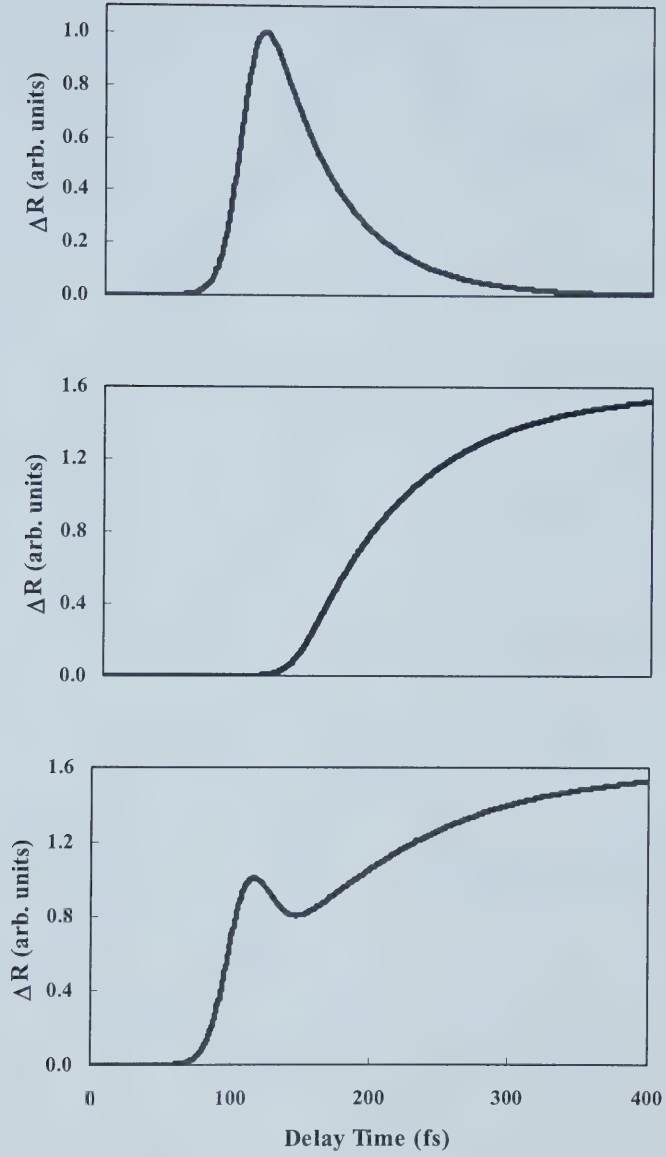


Figure 4.3.3. Plots of the two components of $\gamma_{\perp}(\tau)$, for $A = C_l = C_2 = 1.0$, $\tau_l = 50$ fs, $\tau_2 = 80$ fs, $t_2 = 40$ fs, $t_o = 100$ fs, $\tau_p = 18$ fs. a) The $\gamma_l(\tau)$ component. b) The $\gamma_2(\tau) = \gamma_{2a}(\tau) + \gamma_{2b}(\tau)$ component. c) The sum $\gamma_l(\tau) + \gamma_2(\tau)$. All three plots are normalized to c).

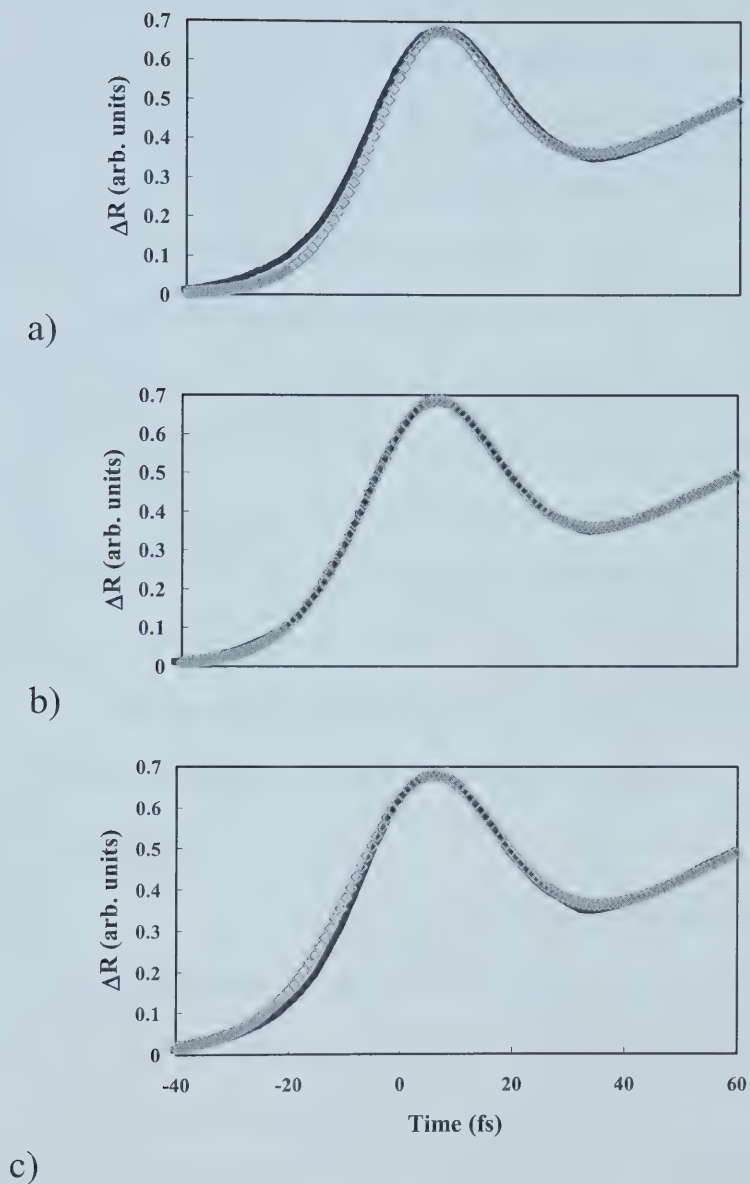


Figure 4.3.4. Determination of the optimum pump/probe pulse width through a fit of data Set 6. a) A pulse width of $\tau_p = 16$ fs does not fit the initial rise or fall of the reflectivity peak. b) The curve is well fit for $\tau_p = 18$ fs. c) A pulse width of $\tau_p = 20$ fs fits neither the initial rise nor fall of the reflectivity peak.

initial portion of the reflectivity rise is not exactly fit. The best fit must, therefore, be decided on how well the rest of the experimental reflectivity curve is followed by the theoretical fit. Clearly, of the three fits, the one for $\tau_p = 18$ fs provides the best correspondence to the first reflectivity peak as neither the curve for $\tau_p = 16$ fs or 20 fs adequately matches the experimental curve in this region.

Shown in Figure 4.3.5 are the numerical fits to the 4 sets of experimental data previously shown in Figure 4.3.1. In each plot a high degree of coincidence between experimental data and theoretical fit is apparent, with only minor discrepancies visible at the highest (Set 1) and the lowest densities (Set 11 *[not shown]* and Set 12). The high quality of the fitting allows for meaningful extraction of the exponential time constants τ_1 and τ_2 , the first of which is plotted in Figure 4.3.6. A clear density dependence of the first decay time, τ_1 , is apparent, with decay times for all measured carrier densities satisfying $\tau_1 < 20$ fs. This density dependence can be with a power law dependence:

$$\tau_1(N) = 23.7 N^{-0.43}. \quad (4.3.10)$$

The ultrafast character of τ_1 in concert with the nature of the density dependence suggests a similarity with the momentum dephasing seen in GaAs by other groups. [3,4]. Both groups measured dephasing times, τ_m , which followed relations close to that seen here with, $\tau_m = 27.2 N^{-0.3}$ via photon echo measurement [3] and $\tau_m = 23.2 N^{-0.36}$ via polarization rotation measurement [4]. The behaviour of the momentum dephasing time, for high carrier concentrations, is expected to show a density dependence due to the various scattering processes which may occur: [3]:

$$\tau_m \propto N^{-1} S(N), \quad (4.3.11)$$

where: $S(N)$ is the density dependence of the scattering effect. For pure Coulomb

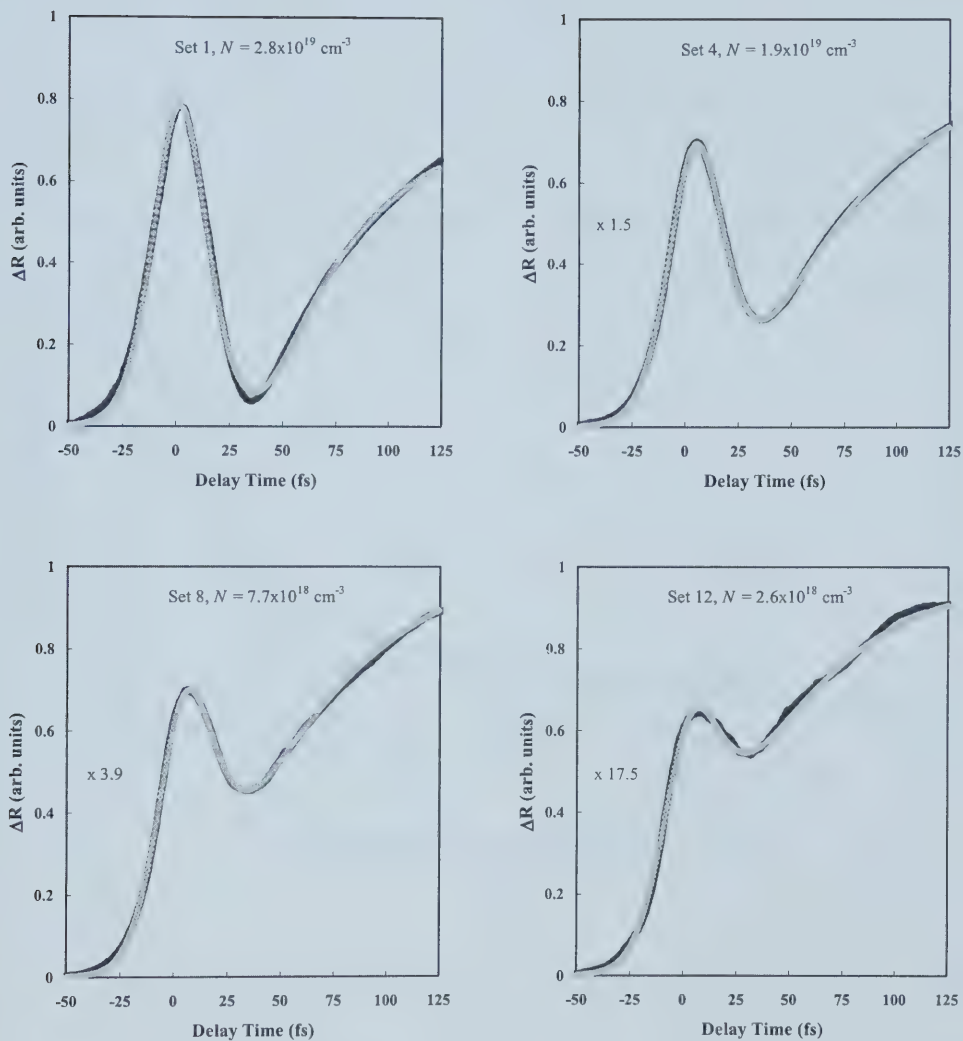


Figure 4.3.5. Theoretical fit (grey diamonds) to four of the 12 data sets (black) via the model proposed in Section 4.3.2. There is an excellent correspondence between theoretical and experimental curves, deviations appearing only at the highest (Set 1) and lowest (Set 12) density.

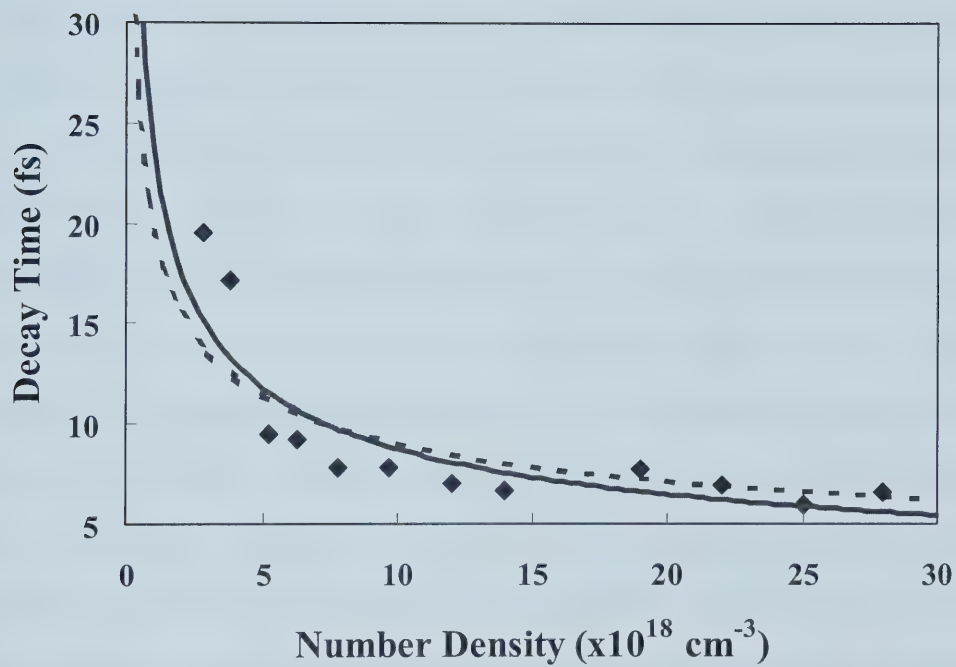


Figure 4.3.6. The density dependence of the exponential time constant, τ_l , utilised to fit the initial reflectivity changes. The solid line represents the best power law fit to the data, $\tau_l(N) = 23.6 N^{-0.43}$, and the density dependence expected for pure Coulomb scattering, ($\tau_l(N) \propto N^{-1/3}$) is show for reference (dotted line).

scattering in the non-degenerate case, $S(N) = N^{2/3}$; thus, the works of reference 3 and 4 agree well with this theory while the current study differs slightly from this form. The apparent dissimilarity may have to do with differences in the density regimes under study, as both referenced works investigate densities below $N = 7 \times 10^{18} \text{ cm}^{-3}$. For carrier concentrations $N > 10^{18} \text{ cm}^{-3}$ in GaAs the photo-excited electron-hole plasma may become somewhat degenerate, hence, the above approximation no longer holds and another more robust theory must be utilised. Another issue is the use of a common pump and probe pulse width in the model, even though the probe is approximately twice the duration of the pump. This will likely affect the values of τ_l extracted from the fit, especially for decay times significantly less than the probe pulse duration. Nonetheless, the conclusion drawn is that τ_l represents the momentum dephasing time, τ_m , which results from the initial carrier-carrier scattering that occurs immediately upon photo-excitation. In this regime, as mentioned in section 2.2.5, the average energy of the carrier distributions remains unaltered but the shape of the distributions will evolve from the initial photo-generated form. The effect of this redistribution will be to empty states within the $\mathbf{k}$ -space region measured by the probe beam that had recently been occupied, thereby reducing the reflectivity.

The density dependence of the second time constant, τ_2 , is shown in Figure 4.3.7. Due to the primary importance placed on the extraction of τ_l , the fit was not extrapolated to great enough delay times to obtain entirely accurate time constants for the four highest density data sets. Nonetheless, the timescale of the rise can still provide useful information on the present dynamics. As each of the rise times, τ_2 , are less than 100 fs there are very few interaction which may occur to alter the carrier distributions, hence,

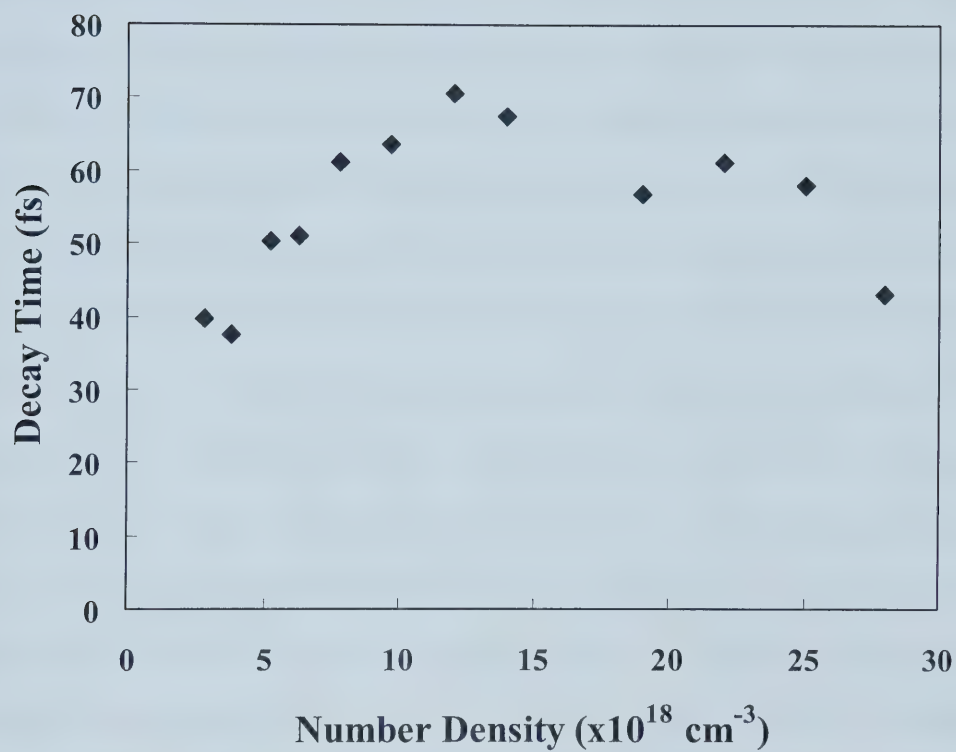


Figure 4.3.7. The density dependence of the exponential time constant, τ_2 , utilised to fit the longer timescale reflectivity rise.

measured reflectivity signal. A prime candidate is electron-heavy hole scattering for the following reason. Interactions between similar charge carrier species, such as hh-hh, lh-lh, e-e, results in very efficient energy transfer as a result of their equivalent masses while conserving the average energy of the individual carrier distributions. This implies that relatively few interactions are needed to randomize an initially non-equilibrium distribution of the stated species, hence, the process is relatively fast. Interaction between the heavy-holes and electrons or light-holes (e-hh or lh-hh), on the other hand, does not conserve the average energy of the individual distributions of each of the scattering species, only the average energy of the total carrier population (electrons and holes) [5]. As well, many interactions are required to effectively transfer energy between particles, due to the large mass differential of the two scattering species ($m_{hh}^* \approx 8 m_e^*$ in GaAs). The result is that the energy transfer leading to equilibrium between the carrier distributions occurs on longer timescales for e-hh interactions than for e-e or h-h scattering. Another process which may influence the form of the reflectivity curve in this temporal regime is optical-phonon emission from the energetic charge carriers. The effect of carrier cooling through phonon emission, hence, relaxation of the carrier energy distributions, has been demonstrated to commence on sub-picosecond timescales [6,7]. Thus, carrier cooling through optical-phonon emission may also play a role in altering the reflectivity of SI-GaAs within the first 300 fs of photo-excitation, as measured here. Clearly, more experimental evidence is necessary in order to conclusively determine the relative importance of these two effects.

4.4 Summary

Utilising a time-resolved pump-probe reflectivity experimental system the temporal evolution of $N = 2.6 \times 10^{18} \text{ cm}^{-3}$ to $N = 2.8 \times 10^{19} \text{ cm}^{-3}$ charge carriers in SI-GaAs on sub-picosecond timescales was measured. An empirical model was developed, based on the convolution of the material response with the pump and probe beam profiles, which accounted for the initial peak and subsequent rise in the reflectivity through a coherent and a non-coherent term. A least squares fitting algorithm, complete with numerical integration routine, was implemented in order to extract the initial decay time, τ_l , and ensuing exponential rise time, τ_2 , and produced excellent fits to the experimental data. The resultant number density dependence of the τ_l identifies it as the momentum dephasing time, τ_m , which results from like-mass carrier-carrier scattering, seen by other groups at lower carrier densities [3,4]. A second exponential time constant was explained in terms of electron-heavy-hole scattering and carrier-phonon interactions. While this study lays the ground work for extracting relevant material parameters from reflectivity measurement a more detailed model is necessary to improve the accuracy of the results. At minimum, the inclusion of separate pump and probe pulse durations into the model alone will greatly improve the accuracy of the extracted time constants. Furthermore, a phenomenological model including such factors as the time evolution of the distribution functions of the photo-generated carriers should be developed as the actual form of the material response function is likely more complex than supposed by the current empirical model.

4.5 References

- [1] Yu. A. Goldberg, "Chapter 1: Aluminum Gallium-Arsenide ($\text{Al}_x\text{Ga}_{1-x}\text{As}$)," in *Handbook Series on Semiconductor Parameters*, edited by M. Levinshtein, S. Rumyantsev, and M. Shur, World Scientific Publishing Co. Pte. Ltd., Singapore (1999).
- [2] D. E. Aspen and A. A. Studna, "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs and InSb from 1.5 to 6.0 eV," *Phys. Rev. B* **27**, 985 (1983).
- [3] P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, "Femtosecond Photon Echoes from Band-to-Band Transitions in GaAs," *Phys. Rev. Lett.* **61**, 1647 (1988).
- [4] M. T. Portella, J.-Y. Bigot, R. W. Schoenlein, J.E. Cunningham, and C. V. Shank, "*k*-space carrier dynamics in GaAs," *Appl. Phys. Lett.* **60**, 2123 (1992).
- [5] M. A. Osman and D. K. Ferry, "Monte Carlo investigation of the electron-hole-interaction effects on the ultrafast relaxation of hot photoexcited carriers in GaAs," *Phys. Rev. B* **36**, 6018 (1987).
- [6] P. Lugli, P. Bordone, L. Reggiani, M. Reiger, P. Kovecar, and S. M. Goodnick, "Monte Carlo studies of nonequilibrium phonon effects in polar semiconductors and quantum wells. I. Laser photoexcitation," *Phys. Rev. B* **39**, 7852 (1989).
- [7] H. Kurz, "Femtosecond spectroscopy of hot carrier relaxation in bulk semiconductors," *Semicond. Sci. Technol.* **7**, B124 (1992).

Chapter 5

Plasmon Oscillations in a Photo-conductive Switch

5.0 Introduction

The subject of this chapter is the carrier and lattice dynamics that occur in voltage biased PC switches on sub-picosecond timescales and their influence on ultrafast electrical pulse generation. First, the physical make-up of a PC switch and a common excitation geometry in which ultrashort electrical pulses are generated are explained. The form of the electric field distribution within the PC gap and the mechanisms responsible for ultrashort electrical pulse generation in edge-illuminated PC switches are presented next. This is followed by a discussion of the various phases of high-field charge carrier transport on sub-picosecond timescales. Finally, the chapter concludes with the results of a pump-probe transient reflectivity experiment on the carrier and lattice-induced field changes that occur in the high-field region of an asymmetrically excited PC switch motivated by the work conducted by M. D. Cummings, J. F. Holzman and A. Y. Elezzabi [1,2].

5.1 Photo-conductive Switching and Charge Carrier Transport

The generation of ultrashort electrical transients and the associated radiated fields is currently a field of intense study. In this broad subject area one device has drawn a great deal of attention, the PC switch, as field oscillations in the THz range can be readily generated [3,4]. By definition a PC switch is a light-activated electrical device, which

through direct illumination by pulsed laser light can map an optical signal into an electrical one, hence, has clear applications to telecommunications. Beyond use in the information technology field the sub-picosecond operation of such switches for the generation of terahertz transients has a wide variety of applications including imaging [6], and spectroscopy [7]. Clearly, a detailed understanding of the physics behind the PC switch is necessary in order to exploit the full potential of these devices.

5.1.1 The Photo-conductive Switch

A schematic of a typical PC switch is illustrated in Figure 5.1.1. Often, the PC switch is composed of a semiconducting substrate onto which a metallic electrical structure, a transmission line, is deposited. In this case a coplanar strip line is shown although other transmission line structures may be utilised as the application may warrant. Typically, the switch is voltage biased but, as a result of the electrical gap, an electrical signal does not propagate down the transmission line. By illuminating the PC gap with a light source of photon energy exceeding the semiconductor bandgap energy, a charge carrier density is generated within the gap, which allows electrical transients to propagate along the transmission line. Sub-picosecond electrical transients are often generated through illumination of the entire PC gap via a femtosecond laser oscillator, which effectively shorts out the PC gap on ultrashort timescales. In this scheme, the rise time of the electrical pulse will be limited primarily by the optical pulse duration and switch geometry (i.e. RC characteristics), while the main factor limiting the fall of the electrical pulse is the material dependent recombination time of the underlying substrate. Full gap illumination of a PC switch fabricated on a short lifetime materials has produced

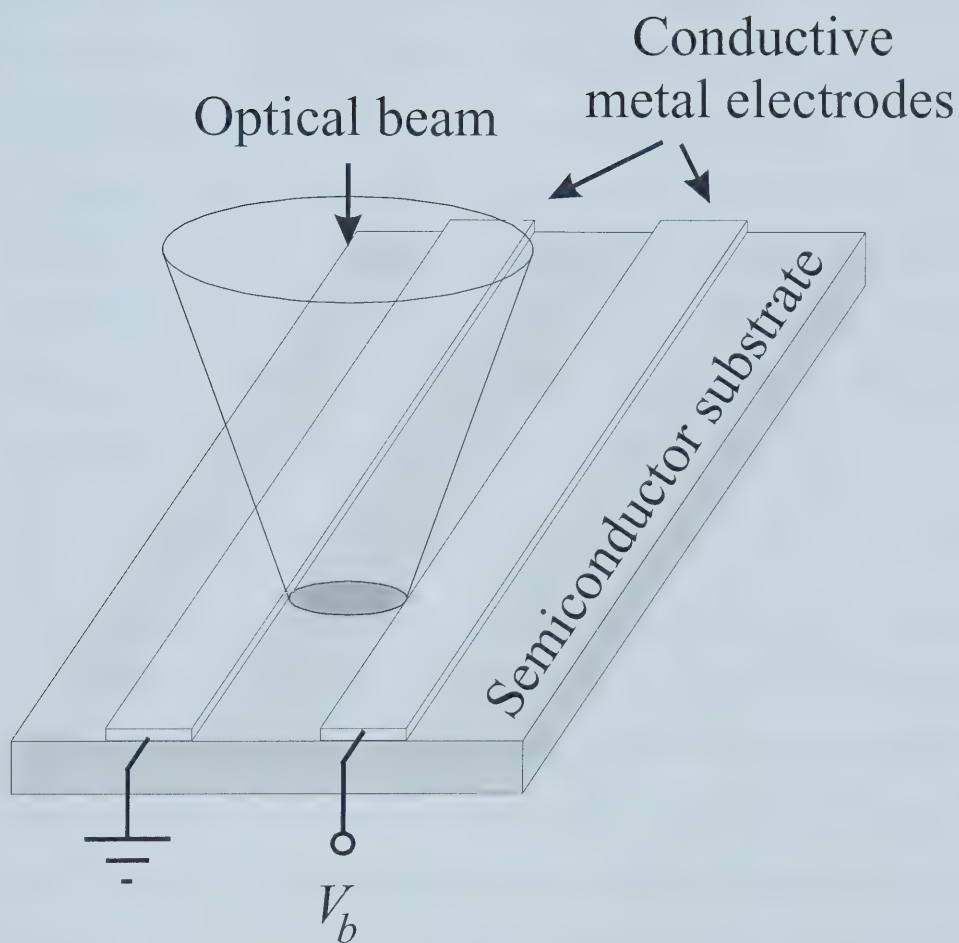


Figure 5.1.1. Schematic of a coplanar transmission line structure consisting of two metal electrodes which have been deposited onto a semiconductor substrate. A potential exists between the electrodes due to the bias voltage, V_b , which is altered by illumination with an above band gap laser pulse.

electrical pulses in the sub-picosecond regime. For example, 600 fs electric transients have been created utilising PC switches fabricated on radiation damaged silicon [8]. While full gap illumination is capable of producing extremely short electrical transients the self-annealing property of radiation-damaged substrates and the material specific recombination time limits their usefulness for mass produced devices [9].

Another means of producing ultrashort electrical signals is known as edge-illumination [10]. In this technique, a pulsed laser is focused onto the switch such that only the edge of the PC gap nearest to the anode is illuminated, which, initially does not fully short out the switch. The manner in which this asymmetric illumination produces a current pulse can be seen from the equation for the displacement current:

$$i(t) = C(t) \frac{dv(t)}{dt} + v(t) \frac{dC(t)}{dt}, \quad (5.1.1)$$

where: $i(t)$ is the current in the PC switch as a function of time, $v(t)$ is the voltage and $C(t)$ is the capacitance. Each term may influence the formation of the photo-generated ultrashort current pulse. The first term can effect electrical pulse creation by inducing an ultrafast change in the voltage across the PC switch, such as through ultrafast charge carrier screening of the applied field, while the second term relies on the ultrashort timescale change of the switch capacitance, such as via ultrafast generation of charge carriers within the gap which effectively reducing the gap size (see Figure 5.1.2). This technique has the benefit of not being limited by the recombination time of the substrate material, with theoretical predictions indicating that sub-100 fs electrical pulses may be realized [11]. Experimentally, edge-illuminated PC switches have produced 250 fs electrical transients [12] and THz pulses as short as 380 fs [13].

While the duration of edge-illuminated electrical transients have the potential to be

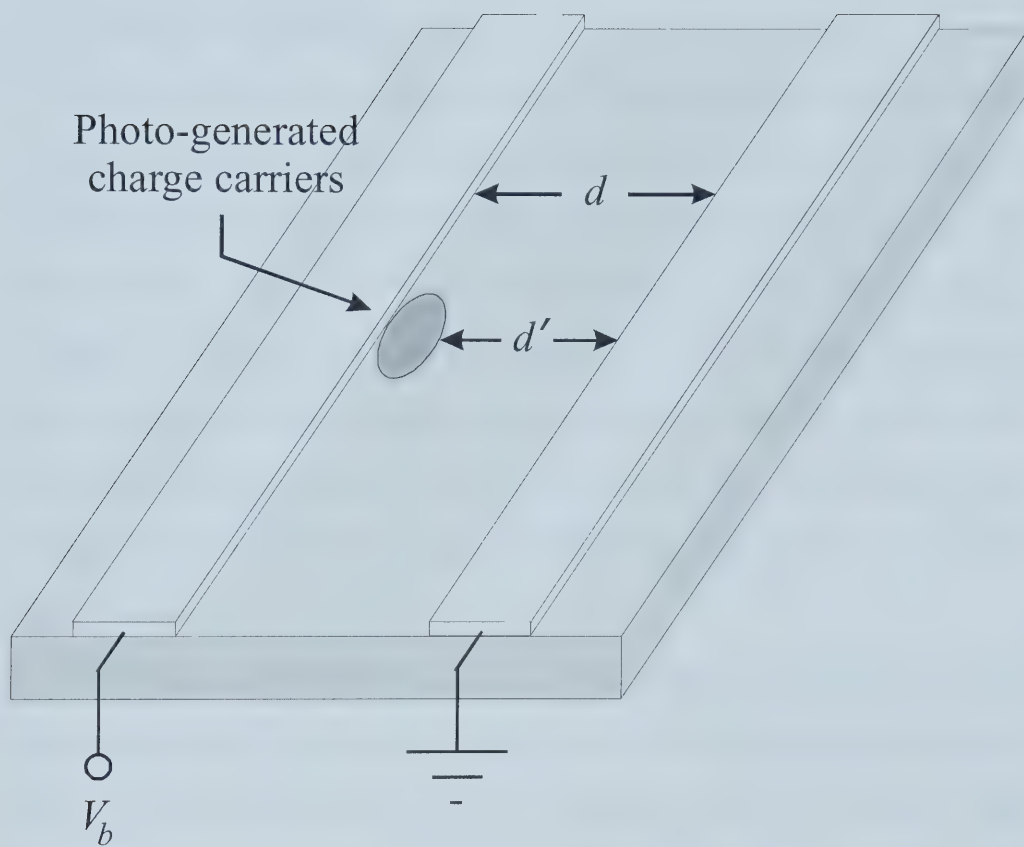


Figure 5.1.2. The effect of charge carrier generation on the capacitance of a PC switch. The initial electrode separation, d , is reduced, to d' , by the generation of charge carriers near the biased electrode.

considerably shorter than those produced by full gap illumination, some debate remains over both the form of the electric field distribution within the gap and the ultimate generation mechanism.

5.1.2 Electric Field Distribution

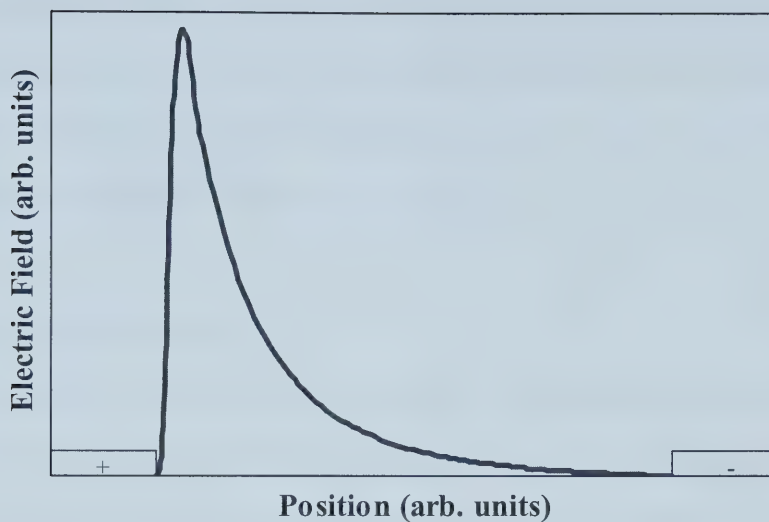
One of the first steps in the determination the ultrashort pulse generating mechanisms in a PC switch is to understand the nature of the electric field distribution within the PC gap. Classically, a calculation of the electric field distribution between the electrodes of a dielectric filled (infinite-plate) capacitor would lead to a solution that was spatially invariant in the region filled by the dielectric. It would be expected that this approximation should hold reasonably well in the gap of the coplanar strip line, for which the distance between the electrodes was much smaller than the length of the transmission line structure. In fact, experimental findings indicate one of two possible field distributions may exist in a PC gap.

The two opinions on the field distribution within the PC gap are predicated on one common observation. Experiments relying on electro-optic sampling [10], THz detection [14] and reflectivity measurement [15,16] all indicate the polarity of the bias voltage drastically affects the signal. If the PC switch is illuminated near an electrode and the bias voltage is positive the detected signal level is, in some cases, orders of magnitude larger than for a negative applied voltage of the same magnitude. This apparent asymmetry has been explained two different ways.

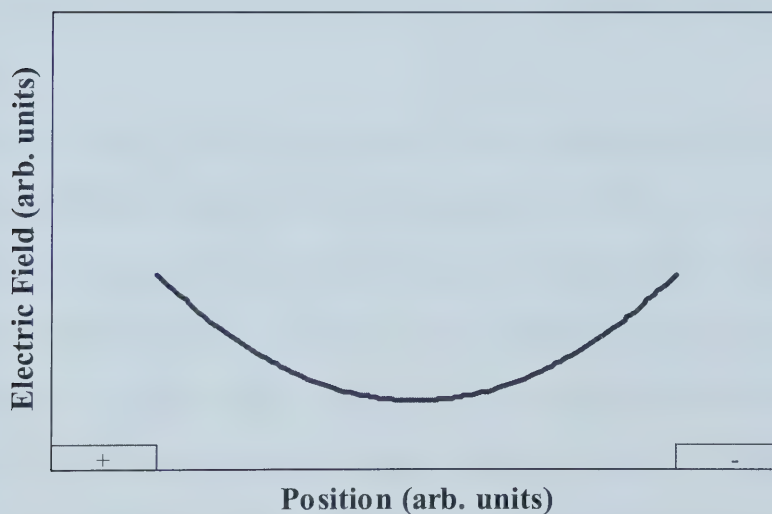
Simulations and experiments in MSM (the semiconductor layer being Si-GaAs) structures [14] indicate the electric field profile within the PC gap is strongly peaked near

the anode. The claim is that this results from the method by which SI-GaAs is made to be semi-insulating. Normally, a native defect, known as EL2, is present in GaAs and acts as a deep donor. In order for the material to become semi-insulating this donor must be compensated for via the introduction of an acceptor impurity, generally carbon. Both experiment and numerical simulations by Ralph et al. [14] indicate the EL2 defect and the compensating impurity coupled with the difference in potential barrier heights at the anode and cathode of a PC switch cause a space-charge region to build preferentially near the anode. It is this space-charge region that ultimately causes the highly peaked electric field distribution, with 90 % of the field concentrated within $5\text{ }\mu\text{m}$ of the anode, for a $80\text{ }\mu\text{m}$ electrode spacing [14]. Other similar pictures, involving preferential carrier trapping or surface ion migration (ex. silicon) [10] are used to explain the asymmetric behaviour in other materials. The field distribution anticipated in this model, as a function of distance between electrodes (after Stephen E. Ralph and D. Grischkowsky [14]), is shown in Figures 5.1.3a.

The alternate point of view is that the electric field distribution is symmetric about the centre of the PC switch, as in Figure 5.1.3b, with the largest field occurring at both electrodes [9,16]. While the field distribution may be equivalent at both the anode and cathode, the behaviour of the photo-injected carriers may be markedly different due to the position dependence of the carrier acceleration in a 2-D electric field. Negatively charged carriers excited near the cathode will be accelerated towards the anode, and into a region of decreasing field, resulting in a diminished acceleration with position. Conversely, negative carriers injected near the anode will be accelerated into a region of increasing field, resulting in an increasing acceleration as the anode is approached. The position



a)



b)

Figure 5.1.3. The two different electrical field distributions postulated to exist between the anode (+) and cathode (-) of a biased photo-conductive switch. a) The asymmetric field distribution picture of S. E. Ralph and D. Grischkowsky [14]. b) The symmetric field distribution picture of U. D. Keil and D. R. Dykaar [9,16].

dependent motion is postulated to be the source of the enhanced response near the anode in PC switches, as carriers at the anode would be more effectively swept out of the probe beam region. This picture has the advantage that it explains the asymmetry in a manner that is independent of the PC switch substrate material.

5.1.3 Generation Mechanisms

As with the nature of the electric field distribution within the PC gap, two different theories exist on the mechanism behind ultrashort electric pulse generation in edge-illuminated switches. These are the voltage breakdown theory, put forth by U. D. Keil and D. R. Dykaar [9,15,16] and the field screening theory, proffered by E. Sano & T. Shibata [11].

Illustrated in Figure 5.1.4 is the time evolution of the voltage across the PC gap in the theory of Keil and Dykaar. Initially, the optically generated carriers near the anode act to cause a voltage drop across the entire switch on a timescale of tens to hundreds of femtoseconds, the transit time for the voltage change across the entire switch. As seen through equation 5.1.1, this ultrafast voltage change across the PC gap results in the generation of an ultrashort electrical transient that may couple to a propagating transmission line mode. On timescales of hundreds of femtoseconds and beyond, as the voltage slowly returns to its initial state, charge carrier screening of the applied field becomes important. This theory is supported by experimental work utilising 5-10 μm gap PC switches on SI-, low temperature (LT) and doped GaAs substrates [16].

In the Sano and Shibata field screening theory, the integral of the electric field (i.e. the voltage) across the entire gap is conserved on ultrashort timescales. Upon photo-

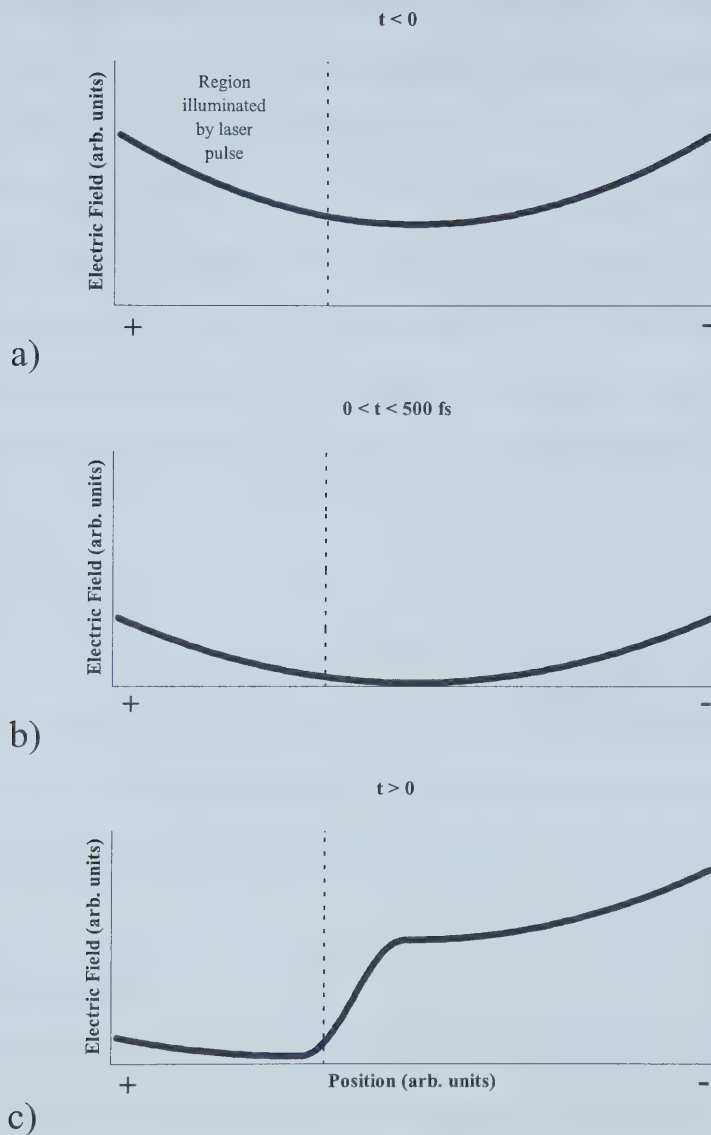


Figure 5.1.4. The temporal evolution of the electric field between the anode (+) and cathode (-) of a PC switch under fs edge-illumination in the voltage breakdown picture. a) Initially, the field is symmetrically distributed between the anode and cathode. b) Photo-excitation results in an immediate voltage drop across the entire PC switch. c) The field distribution returns to the unilluminated state near the cathode but not at the anode.

excitation, as the electrons and holes separate due to the applied field, the induced field between the charge carriers grows as their separation increases until this induced field cancels the applied field. For the case of high fields (tens of kV/cm) and large carrier densities ($\sim 10^{18} \text{ cm}^{-3}$) this cancellation may occur on sub-100 fs timescales. The local reduction of the electric field in the illuminated region is counteracted by an increase in the field elsewhere within the PC gap, as shown in Figure 5.1.5. It is this redistribution of the electric field that is claimed to be responsible for the creation of an ultrashort electrical pulse. Through Maxwell's equations the ultrafast field redistribution results in a displacement current:

$$\mathbf{J}(\mathbf{r}, t) = \frac{\partial [\mathbf{D}(\mathbf{r}, t)]}{\partial t}, \quad (5.1.2)$$

where: $\mathbf{J}(\mathbf{r}, t)$ is the displacement current, and $\mathbf{D}(\mathbf{r}, t) = \epsilon(\omega) \mathbf{E}(\mathbf{r}, t)$. Experimental work with 50 μm coplanar PC switches on SI-GaAs [17], and 15 μm coplanar PC switches on Fe:InP and Si [18], and theoretical simulations [19,20] provide strong evidence for this ultrashort electrical pulse generation mechanism.

5.1.4 Carrier Transport

An understanding of the ultrashort timescale behaviour of charged carriers in an applied field is crucial in the interpretation of PC switch data. This ultrafast behaviour manifests itself through the shape and timescales apparent in the measured signal and provides useful insight into the mechanisms of ultrashort electrical transient generation. The early timescale behaviour of charge carriers in an electric field is critically dependant on the band structure of the underlying semiconductor material. Conduction band side-valleys, variations in mobility with excess carrier energy and breakdown field all shape

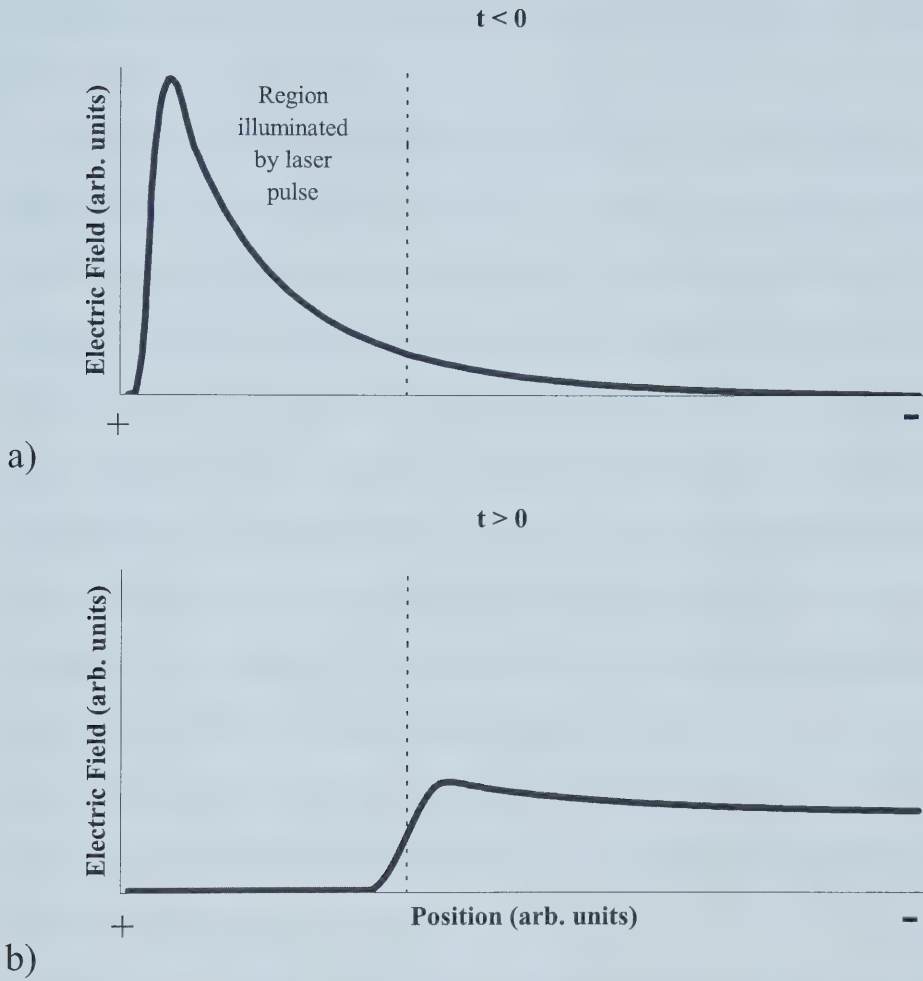


Figure 5.1.5. The temporal evolution of the electric field between the anode (+) and cathode (-) of a PC switch under femtosecond edge-illumination in the field screening picture. a) Before illumination, the field distribution is highly peaked nearest to the anode. b) After illumination, the field within the illumination region decreases and the field within the unilluminated region increases.

the nature of the carrier transport. The following will discuss the four distinct phases in high-field carrier transport in III-V semiconductors that occur on sub-picosecond timescales.

The first phase of high-field carrier transport is only seen in semiconducting material with a direct band gap, such as GaAs [21]. Initially upon photo-excitation, the wavefunctions of the electron and hole in an electron-hole pair remain coherently coupled. Before the carriers are able to separate in the applied field the coherent coupling sets up a macroscopic polarization in the semiconductor, as the electron and hole form a dipole moment, which is oriented in a direction determined by the laser polarization, applied field and quantum selection rules. Hence, this transport phase is known as the instantaneous polarization (IMP) phase, as it occurs immediately upon excitation. The coherence is lost as carriers begin to interact and separate in the applied field and, for large applied fields and/or high carrier densities, disappears on the timescale of the excitation pulse width. This process cannot occur in indirect band gap semiconductors as the phonon-assisted excitation has a randomizing effect on the dipole orientation, leading to a randomly distributed dipole moment.

Upon photo-excitation the electrons and holes begin to separate in the applied field and accelerate ballistically at a rate given by:

$$\mathbf{a}_{e,h} = \frac{q\mathbf{E}_T}{m_{e,h}^*(t)}, \quad (5.1.3)$$

where: $\mathbf{a}_{e,h}$ is the electron/hole acceleration, q is the charge of the electron or hole, $\mathbf{E}_T$ is the total field (sum of applied and screening fields) acting on the carrier and $m_{e,h}^*(t)$ is the time dependent charge carrier effective mass. In high purity materials this ballistic

acceleration phase will continue until the electron has gained enough energy from the field to make a phonon assisted transition to a conduction band side valley favourable. In GaAs, for example, the room temperature energy separation between the Γ -valley and L-valley minima is $\Delta E_{L-\Gamma} = 290$ meV [22]. The approximate time required for the excited carriers to reach this side-valley scattering threshold can be calculated simply through:

$$t = \frac{\sqrt{2m_e^*(t)\Delta E}}{e|\mathbf{E}_{ext}|}, \quad (5.1.4)$$

where: $\Delta E = \Delta E_{L-\Gamma} - \Delta E_{exc}$ is the energy different between the Γ -valley and satellite valley minus the excess energy due to the carrier excitation process. At very high fields, (100 kV/cm in GaAs), the time for the carriers to attain their peak velocity becomes further complicated by quantum collisional effects and the carrier acceleration time falling below the oscillatory period of the scattering phonon [23] and requires the utilisation of Monte Carlo simulations to obtain reasonably accurate values.

The scattering of an electron into a CB side valley signals the end of the carrier acceleration and is the time at which the maximum velocity is reached. Due to the larger effective mass, hence, lower mobility for the carrier in the side-valley its velocity must decrease, as the mobility and velocity are proportional. This is the mechanism behind the velocity overshoot phenomena seen in high-field transport in III-V semiconductors and causes the carriers to decelerate [21]. On timescales of 100-500 fs the carriers reach the final stage of carrier transport and propagate at a steady state velocity.

Measurements of the properties of these four phases in GaAs, such as the relevant timescales, displacement and velocity of the charge carriers, can be found in references. 21 and 23.

5.2 Experimental Observations in Biased Photo-conductive Switches

The purpose of this section is to examine the time-resolved pump-probe reflectivity measurements of the carrier and lattice dynamics produced in an edge-illuminated PC switch. This section opens with a detailed outline of the experimental set-up and sample characteristics utilised. A time domain reflectivity signal, showing a THz modulation on a more slowly varying background, is then analysed in the context of charge carrier and lattice-polarization induced field screening. The THz oscillations are shown to result from coupled plasmon-phonon modes, signifying lattice effects may play a prominent role in the field screening dynamics of edge-illuminated PC switches.

5.2.1 Sample Characteristics

A representation of the coplanar transmission line structure utilised in this experiment is shown in Figure 5.2.1. The underlying substrate consists of an $\sim 620\text{ }\mu\text{m}$ thick, [100] oriented SI-GaAs sample, of resistivity, $\rho = 5 \times 10^7\text{ }\Omega\cdot\text{cm}$, which is polished to optical quality. As gold does not bond well to most semiconductor materials the conductive gold layer, 150 nm thick, is deposited on top of a 50 nm thick adhesive titanium layer. The resultant structure consists of two $100\text{ }\mu\text{m}$ wide Ti/Au lines separated by a $100\text{ }\mu\text{m}$ gap. The substrate is optically glued to a partitioned copper board and the electrodes of the coplanar transmission line are indium bonded to it. Two wires are then soldered to the board and attached to a BNC connector to facilitate interface with the voltage supply. A synopsis of the characteristics of the GaAs substrate can be found in Table 5.1.

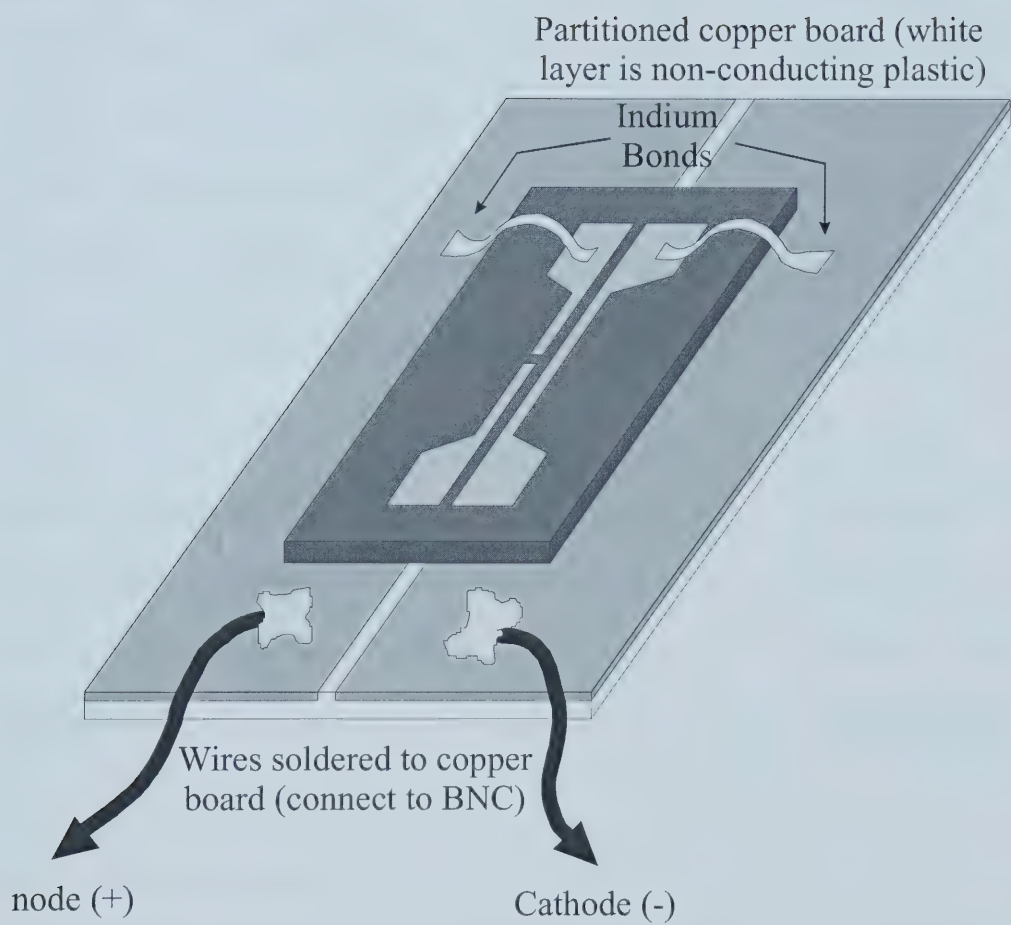


Figure 5.2.1. Schematic of the photo-conductive switch utilised in all experiments.

Table 5.1. Relevant material characteristics of SI-GaAs

Parameter	Symbol	Value
Band gap energy ($T = 300$ K)	E_g	1.424 eV [22]
X-valley energy (above E_g at $T = 300$ K)	$\Delta E_{X-\Gamma}$	290 meV [22]
L-valley energy (above E_g at $T = 300$ K)	$\Delta E_{L-\Gamma}$	480 meV [22]
Γ -valley electron effective mass	m_e^*	$0.063 m_e$ [22]
X-valley electron effective mass (conduction)	m_{eX}^*	$0.27 m_e$ [22]
L-valley electron effective mass (conduction)	m_{eL}^*	$0.11 m_e$ [22]
Heavy-hole effective mass	m_{hh}^*	$0.51 m_e$ [22]
Light-hole effective mass	m_{lh}^*	$0.082 m_e$ [22]
Absorption depth at 810 nm	δ	~ 800 nm [24]
Intrinsic carrier concentration ($T = 300$ K)	N_i	$2.1 \times 10^6 \text{ cm}^{-3}$ [22]
Breakdown Field	$ \mathbf{E}_b $	~ 400 kV/cm [22]

5.2.2 Experimental Set-up

A summary of the experimental parameters is catalogued in Table 5.2. The basic optical set-up utilised in this transient pump-probe reflectivity experiment is nearly identical to that described in Chapter 3, and the experiment is performed at room temperature. The Ti:Sapphire oscillator which outputs $\tau_p = 10$ fs pulses centred at $\lambda_o = 810$ nm at an 80 MHz repetition rate (Ti:S1), served as the laser source for this

Table 5.2. Experimental parameters for PC switch measurement

Parameter	Symbol	Value
Laser centre wavelength	λ_o	810 nm
Output laser pulse duration	τ_p	10 fs
Pump spot diameter	$2w_{pump}$	$\sim 20 \mu\text{m}$
Probe spot diameter	$2w_{probe}$	$\sim 20 \mu\text{m}$
Pump angle of incidence	θ_{pump}	$\sim 0^\circ$
Probe angle of incidence	θ_{probe}	$\sim 10^\circ$
Pump power	P_{pump}	77 mW
Measurement resolution	τ_{res}	28 fs
Bias voltage amplitude	V_b	90 V _{p-p}
Bias voltage modulation frequency	f_b	66.917 kHz

experiment. Both the pump and probe beams are focused onto the sample via the same gold coated parabolic mirror of 5.08 cm focal length to spot diameters of no larger than $20 \mu\text{m}$. The probe beam angle of incidence $\theta_{probe} \approx 10^\circ$ is relative to the normally incident pump beam, therefore, we estimate our temporal resolution to be, $\tau_{res} = 28$ fs. For the duration of the experiment the pump power is maintained at, $P_{pump} = 77$ mW, and the pump-to-probe power ratio is fixed at 10:1. Both spots are focused onto the region near the anode such the gold contact is partially illuminated (≈ 30 % of the focal spot area) to obtain maximal overlap between the PCS high field region and the peak intensity of the

focal spot. In order to enhance signal detection the probe beam polarization was oriented in the direction of the biasing field (i.e. $\mathbf{E}_{probe} \parallel \mathbf{E}_{ext}$) [15,16].

The bias voltage for the transmission line is provided by a Wavetek 178, 50 MHz programmable waveform synthesizer which outputs a $4 V_{p-p}, f_{bias} = 66.917$ kHz signal. In order to achieve large field strengths in the PC switch, this voltage is stepped up via a homemade $\sim 20:1$ voltage transformer to $90 V_{p-p}$. Instead of lock-in detection of the modulation created by optical beam chopping, the bias voltage frequency is utilised as the modulation source for two reasons. First, the higher frequency of detection, over the 1.4 kHz used for our optical beam chopper, and high degree of voltage/frequency stability of the Wavetek function generator allow for enhanced signal-to-noise levels. Second, only signals resulting from changes in the bias voltage, such as carrier-induced field screening processes, will be detected. Therefore, the small reflectivity signals resulting from field screening processes ($[\Delta R/R]_{screened} \sim 10^{-5} - 10^{-6}$) are not swamped out by the much larger non-field related carrier induced reflectivity changes ($[\Delta R/R]_{unbiased} \sim 10^{-2} - 10^{-3}$) which are present without biasing. This detection method allows measurement of reflectivity changes as small as $\Delta R/R = 10^{-6}$.

5.2.3 Results and Discussion

A time-resolved reflectivity signal resulting from the ultrafast generation of $5.6 \times 10^{18} \text{ cm}^{-3}$ electron-hole pairs in the high field region near the anode of the PC switch is shown in Figure 5.2.2. The reflectivity curve exhibits a strong THz modulation superimposed on a more slowly varying background, all of which relates to the change in the local electric field within the probe spot. Before delving into the oscillatory character of the curve, the

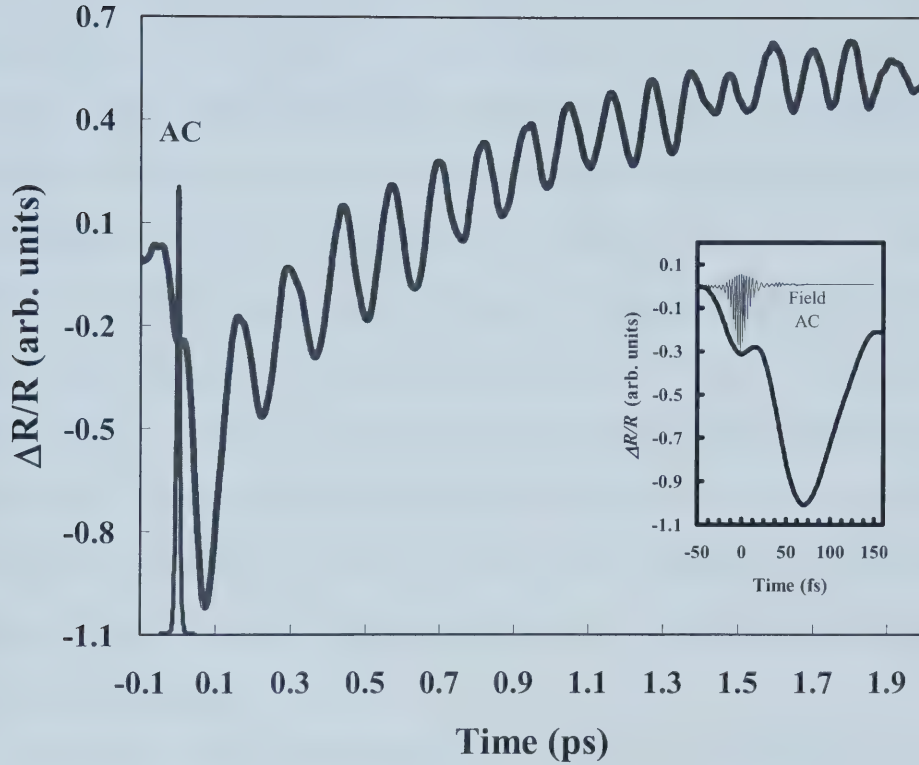


Figure 5.2.2. Time-resolved reflectivity signal resulting from the photo-injection of $N = 5.6 \times 10^{18} \text{ cm}^{-3}$ charge carriers near the anode of a SI-GaAs PC switch under an applied bias voltage of $90 V_{p-p}$ with the pump-probe intensity autocorrelation (AC) shown to indicate the zero time. In the inset, the reflectivity curve has been expanded about the zero time to illustrate the appearance of the IMP (the field autocorrelation has been inverted for comparison).

nature of the background component of the signal should be discussed.

Immediately at the pump-probe overlap time the transient reflectivity curve contains a small decrease in reflectivity, as shown in the inset of Figure 5.2.2. This indicates that the applied electric field is screened on the timescale of the pump-probe overlap and is, therefore, closely related to the charge carrier generation process. The generation of a coherent electron-hole pair on ultrashort timescales leads an instantaneous macroscopic polarization within the crystal, as explained in section 5.1.4. The coherent electron-hole wavefunction creates a macroscopic dipole moment, hence, polarization that is oriented so as to screen the applied field. As the reflectivity signal is related to the changes in the applied field as per equation 3.5.6, this field screening event leads to the observed dip in the reflectivity signal. The ultrafast disappearance of the IMP signal, nearly within the pump-probe overlap time, is a result of the large carrier density and large applied field within the illuminated region causing the rapid loss of coherence through scattering and electron-hole separation.

The IMP is, in fact, superimposed upon a larger change in the time-resolved reflectivity signal that peaks ~ 70 fs after the zero time. This may be attributed to the ballistic acceleration of the electrons and holes which acts to screen the applied electric field on ultrashort timescales as the carriers move in opposite directions, causing a reduction in the measured reflectivity signal. The ballistic acceleration phase ends when the electrons acquire enough energy to scatter out of the high mobility Γ -valley into the lower mobility conduction band L- and X-valleys. Utilising equation 5.1.4 and the values in Table 5.1, an estimate on the field strength in the high field region of the PC switch can be made, assuming most of the electrons scatter into the L-valley within 70 fs of

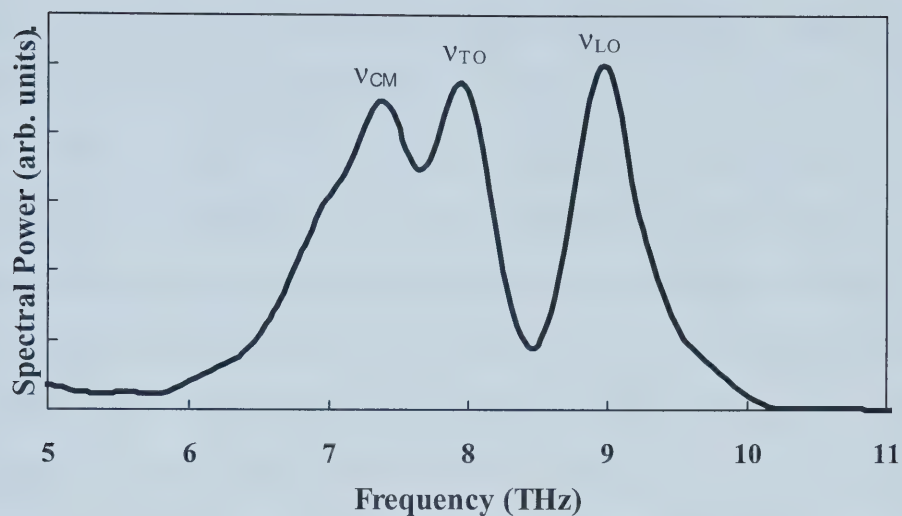
photo-excitation. Thus, the average applied field within the pump spot is calculated to approximately be $E_{ext} \approx 45$ kV/cm, which is ten times the expected value in the case of an electric field distributed uniformly across the gap. This indicates the field distribution is highly asymmetric, with a peak near to the anode.

The large reflectivity change centred at 70 fs and of width, $\Delta\tau_R \approx 80$ fs, corresponds to a reduction of the total electric field within the pump spot as a result of charge carrier-induced screening. Hence, this corresponds to an ultrafast electrical transient within the PC switch that may be able to couple to a propagating transmission line mode. As per the discussion in section 3.5, the change in reflectivity due to electronic induced field screening typically is proportional to the square of the applied field, for probing energies near E_g . Thus, assuming the electrical pulse has a Gaussian temporal shape for simplicity, the duration of the accompanying electric field transient would be anticipated at $\Delta\tau_E \approx 110$ fs, which is near the minimum expected by the theory of Sano & Shibata [11]. However, the coupling of this electric field transient to a propagating transmission line mode combined with the temporal limitations of measurement techniques, such as electro-optic sampling, will result in significant broadening of the measured electric pulse duration [25].

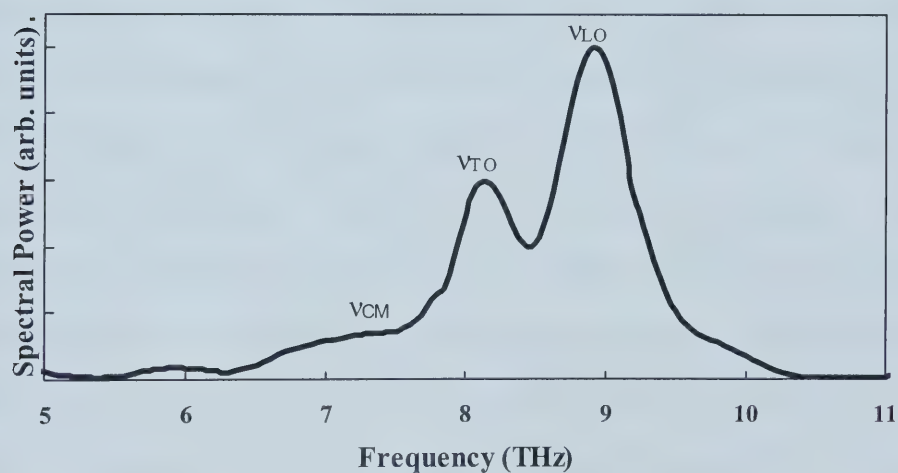
On longer timescales the background reflectivity exhibits a slow variation, on a timescale of ~ 800 fs. A crude calculation, utilising the acceleration formula (equation 5.1.3) under the assumption of an unscreened driving field of magnitude $|E_T| = 45$ kV/cm, and taking into account scattering to the lower mobility side valleys at time $\tau = 70$ fs, shows the carriers are only able to move a small fraction ($<5\%$) of the electrode spacing within 1 ps of photo-excitation. Thus, even under this greatly exaggerated field condition

it appears unlikely that the longer timescale field redistribution is a direct result of charge carrier screening. The time for an electric field transient to propagate $100\text{ }\mu\text{m}$, through the GaAs substrate, is $\sim 1\text{ ps}$. Thus, this information may be interpreted as follows: initially upon photo-generation the charge-carriers screen the local field within the pump spot, decreasing the effective PC gap size and generating the 110 fs electrical transient. Within $\sim 1\text{ ps}$ this field screening information propagates across the area between the electrodes, causing a redistribution of the electric field across the entire switch and, hence, the observed behaviour.

In order to uncover the nature of the oscillatory portion of the reflectivity signal of Figure 5.2.2, a Fourier transform of the time domain data, for times, $\tau > 70\text{ fs}$ after photo-excitation, is performed. As shown in Figure 5.2.3a, three frequency peaks appear at $\nu_1 = 7.4\text{ THz}$, $\nu_2 = 8.0\text{ THz}$, and $\nu_3 = 8.8\text{ THz}$, in contrast to the two modes expected in the plasmon-phonon coupling picture for a homogenous carrier density within the probing region [25-27]. The two highest frequency modes, ν_2 and ν_3 , can be identified from the plasmon-phonon dispersion curve specific to GaAs (Figure 5.2.4). The value of the frequency peak centred at $\nu_3 = 8.8\text{ THz}$ is in good agreement with the bare LO-phonon frequency of $\nu_{LO} = 8.76\text{ THz}$ [25], corresponding to the low plasma density limit of the L_+ mode. In addition, the peak at $\nu_2 = 8.0\text{ THz}$ agrees well with previous measurements of the screened LO-phonon mode frequency (= TO frequency) of $\nu_{TO} = 8.06\text{ THz}$, which is the limiting value of the L_- branch at high carrier densities. It is the phonon-like behaviour of both of these modes, due to weak coupling between the plasmon and phonon motion, which allows for the oscillations to persist for several picoseconds after excitation [28,29], as evidenced in the time domain signal of Figure 5.2.2.



a)



b)

Figure 5.2.3. a) Fourier transform of the time domain reflectivity signal, indicating three prominent frequency components make up the signal. b) Fourier transform of the reflectivity signal, for delay times greater than 470 fs after charge carrier photo-excitation.

The dispersion relation plotted in Figure 5.2.4 demonstrates that at a single, uniform carrier density the two above mentioned plasmon-phonon modes cannot co-exist. Therefore, an explanation in terms of the non-uniform intensity profile of the pump and probe spots is required. As a result of the approximately Gaussian spatial intensity distribution of the pump beam, the photo-generated charge carrier density is nearly homogeneous in a small region about the centre of the excitation spot, as measured by the probe beam. In this high density region, for which $N = 5.6 \times 10^{18} \text{ cm}^{-3}$, the L₋ branch (point A in Figure 5.2.4) exhibits a long decay time due to its phonon-like character while the L₊ branch (point B in Figure 5.2.4) behaves as a plasmon-like mode, with its associated ultrashort lifetime on the order of the momentum dephasing time [29]. As the L₊ mode behaves like an over-damped oscillator the L₋ mode oscillating at the TO-phonon frequency will dominate the time domain signal measured for this region of the carrier density distribution. Thus, a frequency peak at $\nu_{TO} \approx 8.06 \text{ THz}$ figures prominently in the power spectrum. While the L₋ mode at TO-phonon frequency corresponds to the high carrier density behaviour, the observed LO-phonon frequency must result from a different region of the spatial density distribution. In the wings of the pump spot, where the carrier density drops to $N < 2 \times 10^{17} \text{ cm}^{-3}$, the L₋ mode demonstrates plasmon-like behaviour (region α in Figure 5.2.4), with the frequency varying as the square root of the number density. Therefore, small changes in density, through changes in measurement position, will result in noticeable changes in oscillation frequency. Conversely, in this same density regime the phonon-like L₊ mode has a nearly constant frequency (region β in Figure 5.2.4). As measurement by the probe beam constitutes an average over the area encompassed by its spatial profile, the different frequency dependences of the L₋ and L₊

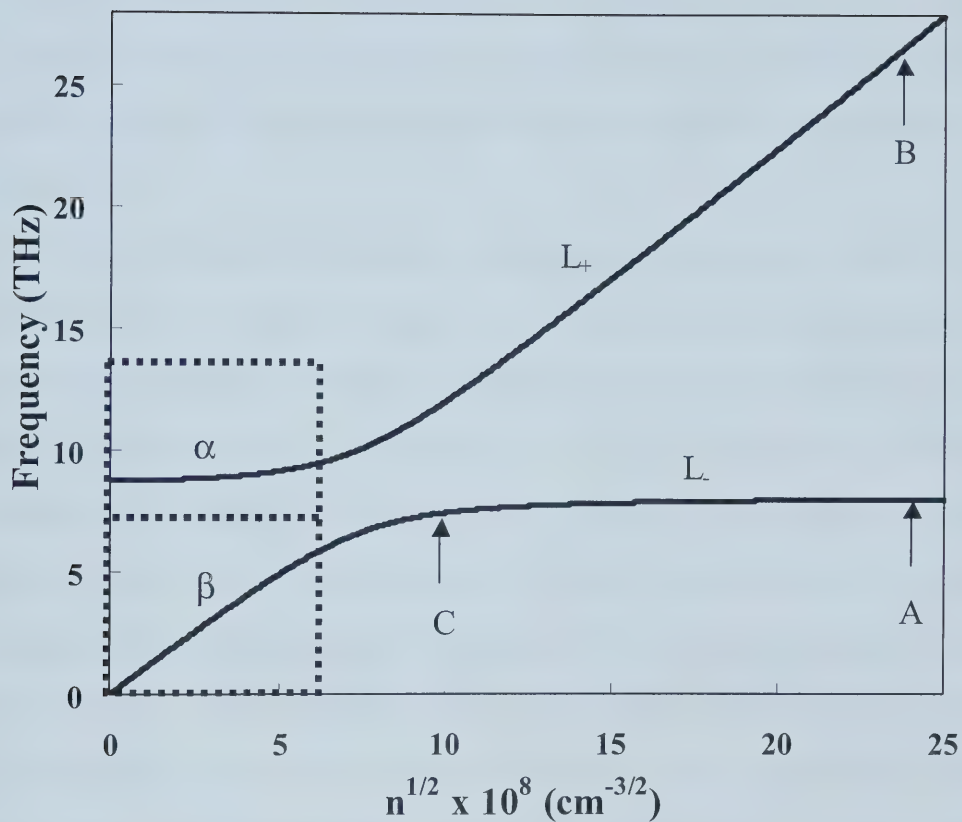


Figure 5.2.4. The plasmon-phonon dispersion curve for GaAs. L_- corresponds to the lower branch mode (lower frequencies) while L_+ is the upper branch mode (higher frequencies). The points A, B, C, and regions α and β are discussed in the text.

modes in the low density regime will influence the detected signal in drastically different ways. The position dependence of the oscillation frequency of the L_- mode leads to a smearing out of this contribution to the measured signal, while the near frequency independence of the L_+ mode results in constructive addition to the response. Thus, the L_+ mode oscillating at the LO-phonon frequency is apparent in the Fourier power spectrum while the L_- mode's contribution is averaged out and, therefore, does not appear.

Unlike the previous two frequency components, the frequency peak centred at $\nu_l = 7.4$ THz cannot be accounted for through pure spatial inhomogeneity of the charge carrier distribution. Consultation of Figure 5.2.4 indicates this frequency corresponds to the L_- plasmon-phonon mode for a carrier density of $N \approx 1 \times 10^{18} \text{ cm}^{-3}$ (point C), with the location of the mode on the dispersion curve indicating a mixed plasmon-phonon character. This strongly coupled behaviour is further observed through a Fourier transform of the reflectivity signal for times beyond 470 fs, as displayed in Figure 5.2.3b. Clearly, within ~ 500 fs of photo-excitation the plasmon-phonon mode is almost completely damped, well less than the time expected for a pure phonon mode (1-4 ps). The origin of this plasmon-phonon mode at 7.4 THz can be explained through consideration of the inhomogeneous nature of the electric field distribution within the PC gap: initially, $N \approx 5.6 \times 10^{18} \text{ cm}^{-3}$ charge carriers are generated in the high-field region of the PC switch and are ballistically accelerated. The resultant polarization created, due to electron-hole separation, leads to a coupling of the charge carriers with the lattice (equations 3.2.4 and 3.2.5) and excites phonon-like modes at the LO- and TO-phonon frequencies. Approximately 70 fs after photo-excitation, a large percentage of the charge

carriers acquire enough energy from the field to scatter out of the central conduction band valley and into the L- and X-valleys [21,23], leaving $N_{\Gamma} \approx 1 \times 10^{18} \text{ cm}^{-3}$ in the Γ -valley. While the momentum randomizing nature of the intervalley scattering process does not allow the carriers in the L- and X-valleys to participate in coherent carrier-lattice oscillations at $\mathbf{q} \approx 0$, the remaining Γ -valley population is not so restricted and oscillates at 7.4 THz. The modes at the LO and TO frequencies are not greatly affected by the intervalley scattering, due to their strong phonon-like behaviour and weak coupling to plasmons, decaying on a timescale of ~ 1.5 ps. Contrary to this, the mixed plasmon-phonon nature of the 7.4 THz mode leads to a rapid decay time of < 500 fs, between that expected for a pure phonon-like and plasmon-like mode.

5.3 Summary

The photo-generation of charge carriers in the high-field region of a PC switch leads to a variety of carrier screening induced material changes which can be seen in bias voltage-locked time-resolved reflectivity measurements. Immediately upon photo-generation, the coherent dipole of the electron-hole pair produces a small field screening event, known as the instantaneous macroscopic polarization, which disappears nearly within the pulse autocorrelation time. The electron-hole pairs quickly separate, so as to screen the bias field, ballistically accelerating until the electrons gain enough energy to scatter to the L- and X-valleys after ~ 70 fs. The ultrafast reflectivity change indicates a field, $|\mathbf{E}_T| \approx 45 \text{ kV/cm}$, accelerates the charge carriers, leading to the postulation that the field in a $100 \text{ }\mu\text{m}$ PC switch is highly peaked near the anode, which supports the asymmetric field picture. The ultrafast screening of the bias field produces a large

reflectivity change near time zero, indicating that an electrical transient as short as 110 fs may be generated through edge-illumination of the PC switch. The participation of the charge carriers in the creation of the ultrashort electrical provides support for the field screening model of ultrashort electrical pulse generation tendered by Sano and Shibata [11]. In addition, the clear influence of the plasmon-phonon coupling suggests that the inclusion of carrier-lattice coupling is necessary to obtain a complete description of electrical pulse generation in PC switches.

5.4 References

- [1] M. D. Cummings, J. F. Holzman, and A. Y. Elezzabi, "Femtosecond carrier dynamics in an asymmetrically excited GaAs photoconductive switch," *Appl. Phys. Lett.* **78**, 3535 (2001).
- [2] M. D. Cummings, J. F. Holzman, and A. Y. Elezzabi, "Ultrafast high-field carrier transport in a GaAs photoconductive switch," *J. Vac. Sci. Technol. A* **20**, 1057 (2002).
- [3] D. H. Auston, K. P. Cheung, and P. R. Smith, "Picosecond photoconducting Hertzian dipoles," *Appl. Phys. Lett.* **45**, 284 (1984).
- [4] A. S. Welington, B. B. Hu, N. M. Froberg, and D. H. Auston, "Generation of tunable narrow-band THz radiation from large aperture photoconducting antennas" *Appl. Phys. Lett.* **64**, 137 (1994).
- [6] B. B. Hu and M. C. Nuss, "Imaging with terahertz waves," *Opt. Lett.* **20**, 1716 (1995).
- [7] M. van Exter, Ch. Fattinger, and D. Grischkowsky, "TeraHz Time Domain Spectroscopy of Water Vapor," *Opt. Lett.* **14**, 1128 (1989).
- [8] M. B. Ketchen, D. Grischkowsky, T. C. Chen, C-C. Chi, I. N. Duling III, N. J. Halas, J-M. Halbout, J. A. Kash, and G. P. Li, "Generation of subpicosecond electrical pulses on coplanar transmission lines," *Appl. Phys. Lett.* **48**, 751 (1986).
- [9] U. D. Keil and D. R. Dykaar, "Ultrafast Pulse Generation in Photoconductive Switches," *IEEE J. Quantum Electron.* **32**, 1664 (1996).

- [10] D. Krökel, D. Grischkowsky, and M. B. Ketchen, "Subpicosecond electrical pulse generation using photoconductive switches with long carrier lifetimes," *Appl. Phys. Lett.* **54**, 1046 (1989).
- [11] E. Sano and T. Shibata, "Mechanism for subpicosecond electrical pulse generation by asymmetric excitation," *Appl. Phys. Lett.* **55**, 2748 (1989).
- [12] U. D. Keil and D. R. Dykaar, "Electro-optics sampling and carrier dynamics at zero propagation distance," *Appl. Phys. Lett.* **61**, 1504 (1992).
- [13] N Katzenellenbogen and D. Grischkowsky, "Efficient generation of 380 fs pulses of THz radiation by ultrafast laser pulse excitation of a biased metal-semiconductor interface," *Appl. Phys. Lett.* **58**, 222 (1991).
- [14] Stephen E. Ralph and D. Grischkowsky, "Trap-enhanced electric fields in semi-insulators: The role of electrical and optical carrier injection," *Appl. Phys. Lett.* **59**, 1972 (1991).
- [15] U. D. Keil, D. R. Dykaar, R. F. Kopf, and S. B. Darack, "Femtosecond reflectivity measurement and second harmonic generation in nonresonant excitation of photoconductive switches," *Appl. Phys. Lett.* **64**, 1812 (1994).
- [16] U. D. Keil, D. R. Dykaar, R. F. Kopf, and S. B. Darack, "Reflectivity measurements of femtosecond carrier and field dynamics in semiconductors," *Appl. Phys. Lett.* **64**, 3267 (1994).
- [17] Sotiris Alexandrou, Chia-Chi Wang, Roman Sobolewski, and Thomas Y. Hsiang "Generation of Subpicosecond Electrical Pulses by Nonuniform Illumination of GaAs Transmission-Line Gaps," *IEEE J. Quantum Electron.* **30**, 1332 (1994).

- [18] Chia-Chi Wang, Marc Currie, Roman Sobolewski, and Thomas Hsiang, "Subpicosecond electrical pulse generation by edge-illumination of silicon and indium phosphide photoconductive switches," *Appl. Phys. Lett.* **67**, 79 (1995).
- [19] Xing Zhou, "Ensemble Monte Carlo Modeling of High-Field Transport and Ultrafast Phenomena in Compound Semiconductors," PhD thesis, Department of Electrical Engineering, University of Rochester (June 1990).
- [20] Xing Zhou, Sotiris Alexandrou and Thomas Y. Hsiang, "Monte Carlo investigation of the intrinsic mechanism of subpicosecond pulse generation by nonuniform illumination," *J. Appl. Phys.* **77**, 706 (1995).
- [21] B. B. Hu, E. A. de Souza, W. H. Knox, J. E. Cunningham, M. C. Nuss, A. V. Kuznetsov, and A. L. Chuang, "Identifying the Distinct Phases of Carrier Transport with 10 fs Resolution," *Phys. Rev. Lett.* **74**, 1689 (1995).
- [22] Yu. A. Goldberg, "Chapter 1: Aluminum Gallium-Arsenide ($\text{Al}_x\text{Ga}_{1-x}\text{As}$)," in *Handbook Series on Semiconductor Parameters*, edited by M. Levinshtein, S. Rumyantsev, and M. Shur, World Scientific Publishing Co. Pte. Ltd., Singapore (1999).
- [23] A. Leitenstorfer, S. Hunsche, J. Shah, M. C. Nuss, and W. H. Knox, "Femtosecond high-field transport in compound semiconductors," *Phys. Rev. B* **61**, 16 642 (2000).
- [24] D. E. Aspen and A. A. Studna, "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs and InSb from 1.5 to 6.0 eV," *Phys. Rev. B* **27**, 985 (1983).
- [25] A. V. Kuznetsov and C. J. Stanton, "Coherent phonon oscillations in GaAs," *Phys. Rev. B* **51**, 7555 (1995).

- [26] Alex. V. Kuznetsov and Christopher J. Stanton, “Chapter 7: Theory of Coherent Phonon Oscillations in Bulk GaAs,” in *Ultrafast Phenomena in Semiconductors*, edited by Kong-Thon Tsen, Springer-Verlag, New York (2001).
- [27] Muneaki Hase, Shin-ichi Nakashima, Kohji Mizoguchi, and Hiroshi Harima, “Ultrafast decay of coherent plasmon-phonon coupled modes in highly doped GaAs,” *Phys. Rev. B* **60**, 16 526 (1999).
- [28] G. C. Cho, W. Kütt, and H. Kurz, “Subpicosecond Time-Resolved Coherent-Phonon Oscillations in GaAs,” *Phys. Rev. Lett.* **65**, 764 (1990).
- [29] G. C. Cho, T. Dekorsy, H. J. Bakker, R. Hövel, and H. Kurz, “Generation and Relaxation of Coherent Majority Plasmons,” *Phys. Rev. Lett.* **77**, 4062 (1996).

Chapter 6

Coherent Acoustic Phonons in InSb

6.0 Introduction

Introduction of charge carriers into a semiconductor on ultrashort timescales enables the excitation of coherent lattice modes, as discussed in Chapter 4. Once generated, the time evolution of these coherent modes allows for insight into the fundamental physics which governs the lattice. At high carrier densities the lattice can be induced by these carriers to behave in an anharmonic manner, which can lead to lattice instability. Hence, the time-resolved observation of these coherent phonon modes allows for investigation of the mechanisms at work during ultrafast phase transitions and femtosecond laser induced lattice instabilities, not to mention the nature of the carrier-lattice energy exchange processes.

The aim of this chapter is to discuss the time-resolved pump-probe reflectivity experiments that led to the observation of coherent acoustic phonon oscillations in InSb, as reported by M. D. Cummings and A. Y. Elezzabi [1]. First, the experimental system and sample characteristics will be described in detail. This will be followed by a discussion on the appearance of the LA-phonon modes in the reflectivity signal and their frequency domain characteristics. Finally, the observations leading to the conclusion that the lattice is moving towards an unstable regime at fluences well below the material damage threshold will be elucidated.

6.1 Sample Characteristics and Experimental Details

The experiment is performed on a single 500 μm thick InSb sample with surface normal in the [111] direction, polished to optical quality. The sample is unintentionally n-doped, $N_d = 9 \times 10^{13} \text{ cm}^{-3}$, and has a large electron mobility at $T = 77 \text{ K}$ of $\mu_e = 6 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ [2]. Due to the small band gap of InSb with respect to the excitation photon energy of the source laser, $E_g = 0.175 \text{ eV}$ vs. $E_l = 1.53 \text{ eV}$, the photo-generated carriers have an excess energy several times the band gap value ($\Delta E_{exc} \approx 7.7 E_g$). Hence, impact ionization through interband collision processes may lead to a carrier density several times greater than the photo-generated value, as the highly energetic and mobile carriers collide with occupied valence band states. For convenience, all relevant sample characteristics have been catalogued in Table 6.1.

The basic optical set-up utilised in this transient pump-probe reflectivity experiment is identical to that described in section 4.1, for the Ti:S1 oscillator set-up, with all measurements being performed at room temperature. Both the pump and probe beams are focused onto the sample via the same gold coated parabolic mirror of 5.08 cm focal length. The spot sizes at the sample were measured utilising the knife-edge technique. The larger pump spot is slightly elliptical, with a horizontal diameter of 12 μm and a vertical diameter of 8 μm and the smaller probe spot is essentially circular with a diameter of $\sim 6.5 \mu\text{m}$. The probe beam is incident at an angle of $\theta_{probe} \approx 13^\circ$ relative to the normally incident pump beam, with a high degree of overlap between the two beams at the sample. Thus, due to the dispersive effects of the pump-probe beam splitter and APB we estimate our temporal resolution to be, $\tau_{res} = 25 \text{ fs}$. Variation of the pump and probe power is accomplished via rotation of a linear polarizer placed in the source beam

Table 6.1. Relevant material characteristics of the [111]-InSb sample

Parameter	Symbol	Value
Band gap energy ($T = 300$ K)	E_g	0.172 eV [3]
Γ -valley electron effective mass	m_e^*	$0.014 m_e$ [3]
Heavy-hole effective mass	m_{hh}^*	$0.43 m_e$ [3]
Light-hole effective mass	m_{lh}^*	$0.015 m_e$ [3]
Index of refraction at 810 nm	n_c	4.46 [4]
Extinction coefficient at 810 nm	k	0.67 [4]
Absorption depth at 810 nm	δ	96 nm [4]
Intrinsic carrier concentration ($T = 77$ K)	N_d	$9 \times 10^{13} \text{ cm}^{-3}$ [2]
Electron mobility ($T = 77$ K)	μ_e	$6 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ [2]
Electron diffusion coefficient ($T = 77$ K)*	D_e	$1.5 \times 10^5 \text{ cm}^2/\text{s}$
Hole diffusion coefficient ($T = 300$ K)	D_h	$22 \text{ cm}^2/\text{s}$ [3]
Damage threshold fluence	F_d	$15 \text{ mJ}/\text{cm}^2$ [5]

*Value calculated from the electron mobility at $T = 77$ K via the Einstein relation.

before it is split into pump and probe pulses. In this configuration the power is varied over 2 orders of magnitude while the pump-to-probe power ratio is maintained at 10:1. Similar to the GaAs experiment of Chapter 4, differential and lock-in detection is carried out at the frequency of the optical chopper, $f_{\text{chopper}} = 1.4$ kHz. A summary of these experimental parameters is catalogued in Table 6.2.

Table 6.2. Experimental parameters for the InSb measurements

Parameter	Symbol	Value
Laser centre wavelength	λ_o	810 nm
Output laser pulse duration	τ_p	10 fs
Pump spot size (horizontal×vertical axes)	$a_{pump} \times b_{pump}$	$12 \times 8 \mu\text{m}^2$
Probe spot size (horizontal×vertical axes)	$a_{probe} \times b_{probe}$	$6 \times 7 \mu\text{m}^2$
Pump angle of incidence	θ_{pump}	$\sim 0^\circ$
Probe angle of incidence	θ_{probe}	$\sim 13^\circ$
Measurement resolution	τ_{res}	25 fs
Chopping frequency	$f_{chopper}$	1.4 kHz

6.2 Results and Discussion

Shown in Figure 6.2.1 is a set of time-resolved reflectivity measurements, taken for pump energy fluences ranging from $F_{pump} = 20 \mu\text{J}/\text{cm}^2$ to $0.83 \text{ mJ}/\text{cm}^2$. As for GaAs, the processes which shape these transient reflectivity signals depend primarily on the dynamics of the photo-generated charge carriers, with lattice heating also playing a prominent role for longer timescales ($\sim 1\text{-}10$ ps and beyond). An exact determination of the importance of the individual processes that shape these reflectivity curves is difficult due to the large excess energy and the high densities of charge carriers produced here. Certainly, effects such as pump-probe coherence, state- and band-filling, band gap renormalization and free carrier absorption shape the reflectivity curves but the nature of their influence depends strongly on the carrier distribution function and density which are

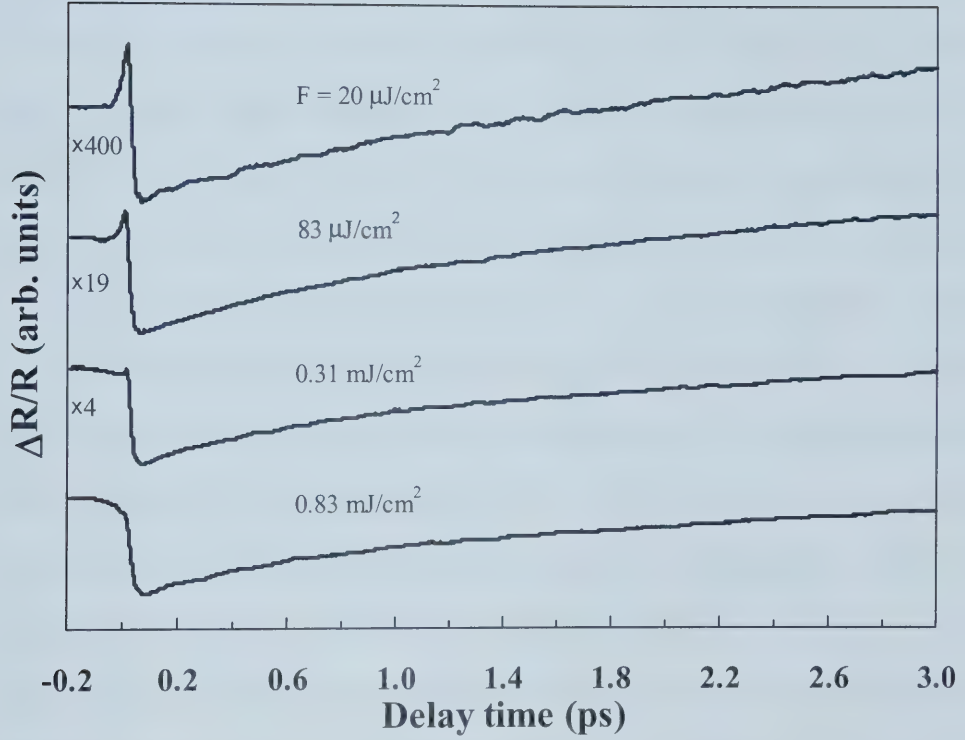


Figure 6.2.1. Transient pump-probe reflectivity measurements of [111]-InSb for energy fluences ranging from $20 \mu\text{J}/\text{cm}^2 \leq F \leq 0.83 \text{ mJ}/\text{cm}^2$.

modified on femtosecond timescales due to the ultrafast diffusion and the multitude of scattering process (carrier-carrier, intervalley, impact ionizing and carrier-phonon). The important point to be made is that carrier effects are the primary mechanisms in the short timescale reflectivity changes in InSb. This fact will be utilised in order to separate the phonon contribution from the charge carrier induced changes at higher energy fluences.

Figure 6.2.2 shows four transient reflectivity curves for increased energy fluences relative to those illustrated in Figure 6.2.1. For each reflectivity signal above the threshold fluence, $F_{pump} > 1 \text{ mJ/cm}^2$, an oscillatory component superimposed on the charge carrier induced background is apparent. In the approximation of linear absorption, $\alpha \approx 1 \times 10^5 \text{ cm}^{-1}$ [4], a threshold fluence value of $F \approx 1 \text{ mJ/cm}^2$ corresponds to a photo-generated charge carrier density of $N \approx 2.5 \times 10^{20} \text{ cm}^{-3}$, while enhancement due to impact ionization may result in a much larger local charge density. As the damage threshold fluence value of $F = 15 \text{ mJ/cm}^2$ at 800 nm with 150 fs optical pulses has been measured by A.M. Lindenberg et al. [5], all fluence values quoted here correspond to <10 % of the damage threshold. Inspection of the reflectivity curves for the three highest fluences in Figure 6.2.2 reveals the oscillation amplitude grows quickly relative to the charge carrier-induced reflectivity background as the pump fluence is increased. The ratio of the maximum reflectivity change, due to charge carrier-induced effects, to the oscillatory portion of the signal varies between approximately $\sim 5\%$, at $F = 1.1 \text{ mJ/cm}^2$, and $\sim 25\%$, at $F = 1.3 \text{ mJ/cm}^2$. The large increase in oscillation amplitude seems to suggest a non-linear dependence on the excitation fluence but more data points are necessary before a strong correlation can be made.

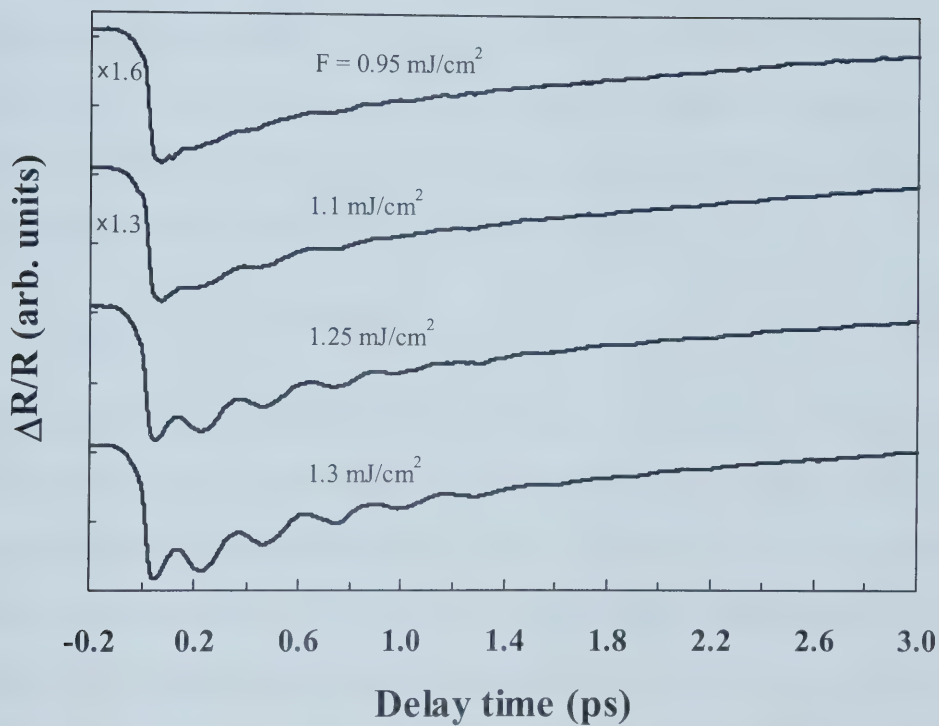


Figure 6.2.2. Transient pump-probe reflectivity measurements of [111]-InSb for energy fluences ranging between $0.95 \text{ mJ/cm}^2 \leq F \leq 1.3 \text{ mJ/cm}^2$. Reflectivity oscillations are evident for energy fluences exceeding 1.0 mJ/cm^2 .

Determination of the nature of and mechanisms behind an oscillatory mode may often be clearly seen through analysis of the frequency spectrum of the mode. Through subtraction of the charge carrier induced component of the three largest fluence reflectivity signals the oscillatory component can be extracted, as seen in Figure 6.2.3. Utilising a custom designed MATLAB program, the Fourier power spectrum for each extracted signal is calculated, as shown in Figure 6.2.4. In each spectrum two frequency peaks are visible. At the lowest energy fluence for which oscillations are visible, $F = 1.1 \text{ mJ/cm}^2$, the frequencies and decay times for the two modes can be determined through an exponentially damped, sinusoidal fitting function of the form:

$$S(\omega, t) = \sum_{i=1,2} A_i e^{-\frac{t}{\tau_i}} \cos(2\pi\nu_i t), \quad (6.2.1)$$

where: $S(\omega, t)$ is the sinusoidal component of the signal, A_i is amplitude coefficient, ν_i is the frequency and τ_i is the decay time for mode i . The Fourier transform of the fitting function places the two frequency peaks at $\nu_1 = 3.75 \text{ THz}$ and $\nu_2 = 4.34 \text{ THz}$. From the phonon frequencies listed in Table 6.3 it is clear that these modes correspond most closely to the LA-phonon modes with $\mathbf{q}$ -vectors oriented in the L- and X- directions in InSb, respectively. The above values are found to be in excellent agreement with the values of $\nu_{LA}(L) = 3.81 \pm 0.06 \text{ THz}$ and $\nu_{LA}(X) = 4.30 \pm 0.10 \text{ THz}$ determined by Price et al. [6]. In addition, the decay times of $\tau_{LA}(L) = 850 \text{ fs}$ and $\tau_{LA}(X) = 550 \text{ fs}$ produced by the fitting function indicate that a sub-picosecond damping mechanism is present in this system. Curiously, the power spectra show no indication of any LO-phonon-plasmon modes that often are generated as a result of photo-Dember [7] or surface fields. The

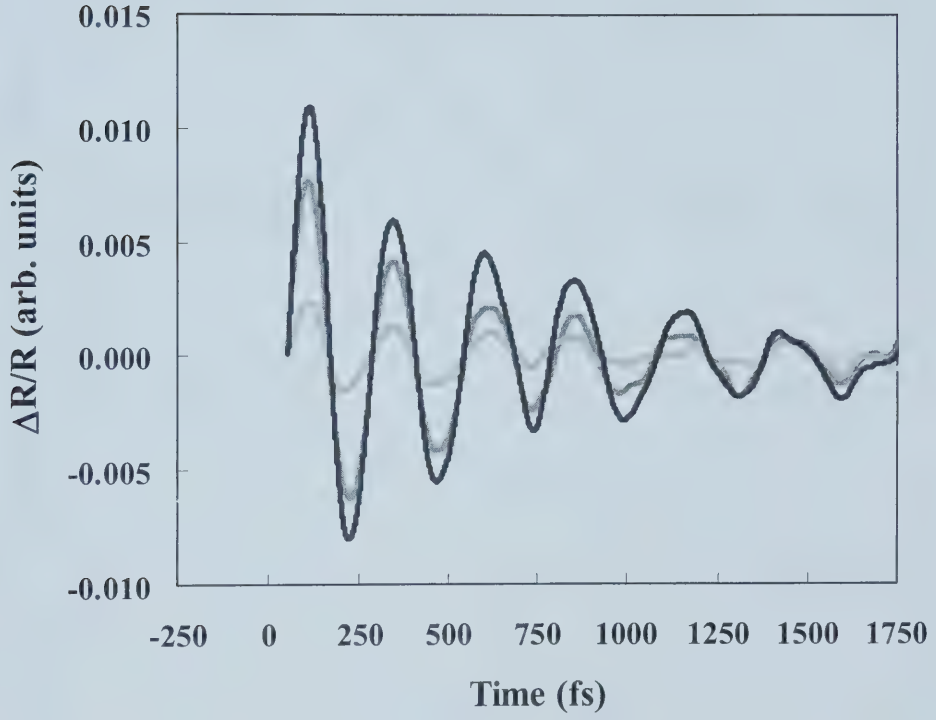


Figure 6.2.3. Oscillations extracted for the three highest energy fluences of Figure 6.2.2. Light grey: $F = 1.1 \text{ mJ/cm}^2$, medium grey: $F = 1.25 \text{ mJ/cm}^2$, and black: $F = 1.3 \text{ mJ/cm}^2$.

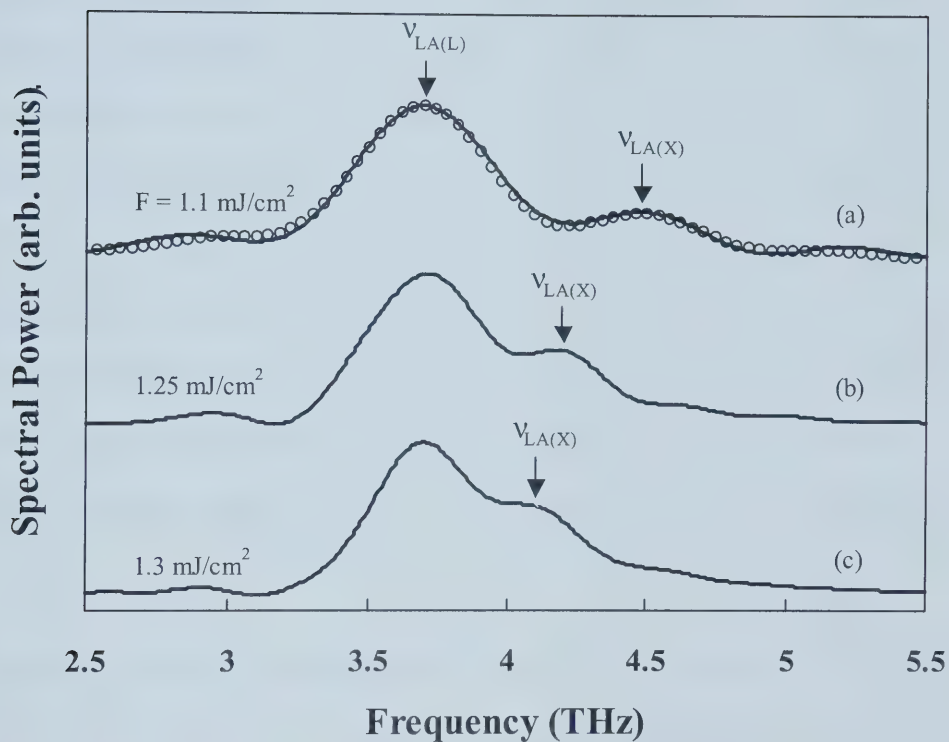


Figure 6.2.4. Fourier power spectra of the extracted oscillations of Figure 6.2.3. The fit (circles) corresponds to the Fourier transform of the function $\sum_{i=1}^2 A_i e^{-t/\tau_i} \cos(2\pi\nu_i t)$, where: $\nu_1 = 3.75$ THz, $\nu_2 = 4.34$ THz, $\tau_1 = 850$ fs and $\tau_2 = 550$ fs. a) $\nu_{LA(L)} = 3.75$ THz, $\nu_{LA(X)} = 4.30$ THz, b) $\nu_{LA(X)} = 4.12$ THz, c) $\nu_{LA(X)} = 4.08$ THz.

Table 6.3. InSb phonon frequencies

Phonon	Symbol	Value
Γ -valley longitudinal optic	$\nu_{LO}(\Gamma)$	5.90 THz
Γ -valley transverse optic	$\nu_{TO}(\Gamma)$	5.54 THz
X-valley longitudinal optic	$\nu_{LO}(X)$	4.75 THz
X-valley transverse optic	$\nu_{TO}(X)$	5.38 THz
<i>X-valley longitudinal acoustic</i>	$\nu_{LA}(X)$	<i>4.30 THz</i>
X-valley transverse acoustic	$\nu_{TA}(X)$	1.12 THz
L-valley longitudinal optic	$\nu_{LO}(L)$	4.82 THz
L-valley transverse optic	$\nu_{TO}(L)$	5.31 THz
<i>L-valley longitudinal acoustic</i>	$\nu_{LA}(L)$	<i>3.81 THz</i>
L-valley transverse acoustic	$\nu_{TA}(L)$	0.98 THz

large photo-excited charge carrier densities produced in this experiment ($5 \times 10^{18} \text{ cm}^{-3} < N < 3.0 \times 10^{20} \text{ cm}^{-3}$) result in correspondingly high plasma frequencies ($37 \text{ THz} < f_{pl} < 290 \text{ THz}$). If any plasmon modes are generated in this system the very high oscillation frequencies would lead to extremely weak coupling with LO-phonon modes, not to mention the extremely short momentum relaxation times of the hot electron-hole plasma would be expected to damp out any coupled mode oscillations on ultrashort timescales.

While the power spectra indicate the oscillatory signals result from the excitation of two separate acoustic phonon modes, more information is needed to determine the generation mechanism for these modes. As mentioned in Chapter 4, the nature of the

driving force behind an excitation, whether impulsive, displacive or other is often indicated by the initial (time zero) phase of the mode. For displacive excitation, as seen through equation 3.1.6, when the oscillation frequency is much greater than the inverse of the dephasing time ($\omega \gg \gamma$) the sine component of the motion becomes negligible, hence, the motion displays a cosine-like dependence at time zero. In the present case the inverse of the dephasing time is significantly smaller than the frequency. Thus, a displacive excitation would be indicated if cosine-like behaviour was observed at time zero while impulsive excitation would be signified by sine-like behaviour. Displayed in Figure 6.2.5 is a fitting of the first 400 fs of the extracted oscillations of Figure 6.2.3 at the three highest fluences, utilising the bi-sinusoidal form of equation 6.2.1. The two oscillatory curves measured at the highest fluence levels are well fit and indicate a cosine-like behaviour for the vibrational modes at the zero time. While the signal taken at the lowest fluence value cannot be fit quite as accurately, due to the small amplitude of the signal, nonetheless, it also appears to behave in a cosine-like manner near the zero time. This observation of an extremum in the oscillation amplitude at the pump-probe zero time strongly implicates a displacive process as the excitation mechanism of the acoustic phonon modes [8-11].

An obvious feature of Figure 6.2.4 is the shift of the LA(X)-phonon central frequency as the pump power density is altered. Increasing the energy fluence above the threshold value for which oscillations are first observed, $F = 1.1 \text{ mJ/cm}^2$, results in an immediate and dramatic red-shift of the frequency of this mode. As the pump fluence is raised from $F = 1.1 \text{ mJ/cm}^2$ to $F = 1.25 \text{ mJ/cm}^2$ a decrease in the phonon frequency, from $\nu_{LA}(X) = 4.34 \text{ THz}$ down to $\nu_{LA}(X) = 4.12 \text{ THz}$, is observed. This trend continues at the highest

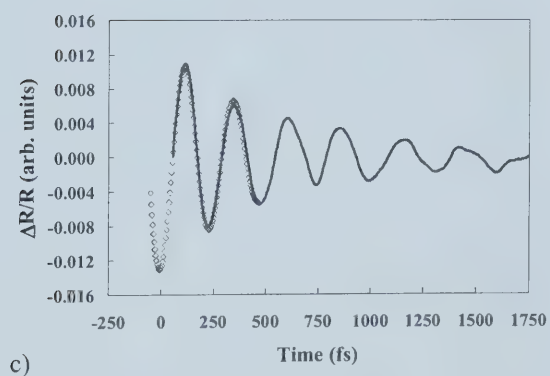
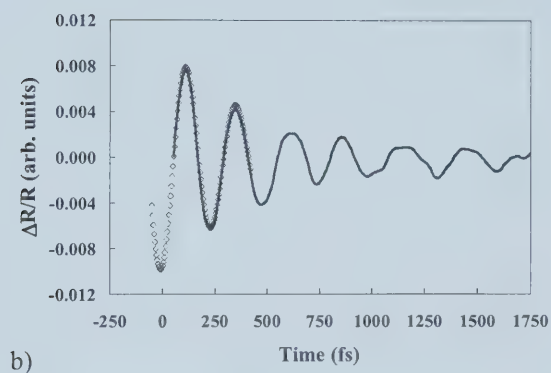
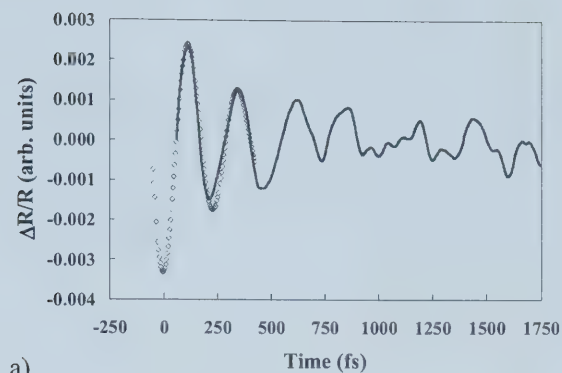


Figure 6.2.5. Fit of the extracted oscillations (from Figure 6.2.3) to a bi-sinusoidal function. The cosine-like behaviour near time zero suggests a dispersive excitation mechanism is at work. a) $F = 1.1 \text{ mJ/cm}^2$, b) $F = 1.25 \text{ mJ/cm}^2$, c) $F = 1.3 \text{ mJ/cm}^2$.

energy fluence, $F = 1.3 \text{ mJ/cm}^2$, at which the LA(X) mode experiences a further downshift to $\nu_{LA}(X) = 4.04 \text{ THz}$. While the frequency of the LA(X)-phonon is a strong function of the illumination fluence, over the same range of power densities the LA(L)-phonon frequency appears to be independent of the excitation fluence and is maintained at $\nu_{LA}(L) = 3.75 \text{ THz}$. The theory of lattice softening and instability put forth by Stampfli and Bennemann [12] may offer some insight into the frequency red-shift observed in this experiment. While much of their work deals with softening of the TA-phonon modes and the role of LO-phonon distortions in enacting a phase change from a diamond or zincblende structure to a non-centrosymmetric state as a result of the generation of a very high charge carrier density, it does not directly address LA-phonon modes. Nonetheless, the reduction in lattice ion bonding energy which accompanies large carrier density photo-excitation, hence, induces TA-phonon mode softening in their model is likely to affect the frequency characteristics of other lattice vibrations. Thus, the behaviour observed here can be readily explained in terms of an anisotropic softening of the InSb lattice, as the lattice restoring forces in the direction X- ($= [100]$) are preferentially weakened due to the perturbative effects of the large charge carrier density while the restoring forces in the L- ($= [111]$) direction are unaffected. The large scale weakening of the interatomic bonds leads to anharmonic oscillations at a frequency lower than the normal harmonic frequency, as per equation 3.4.4. Hence, the LA(X)-phonon mode results from anharmonic oscillations while the LA(L)-phonon mode is due to purely harmonic lattice vibrations.

6.3 Summary

In summary, the data acquired in the course of this experiment leads to the following interpretation of the carrier and lattice dynamics which occur in InSb when illuminated by 10 fs pulses at a central photon energy of 810 nm: for low pump power densities and sub-picosecond timescales the temporal evolution of the dielectric function is primarily governed by charge carrier induced processes. Above a threshold energy fluence of $F \sim 1.0 \text{ mJ/cm}^2$ a sufficient charge carrier density is generated through photo-excitation and impact ionization to alter the potential well in which the lattice ions are normally localized and, therefore, the equilibrium co-ordinate of vibration. Thus, the lattice ions rearrange themselves to increase ionic separation and oscillate about the new equilibrium in the manner expected from the displacive excitation of a classical oscillator system. As the excitation mechanism, the pump-pulse generation of charge carriers, is significantly shorter than the period of the oscillation, coherent phonon modes are generated. The two observed phonon mode frequencies, as measured at the lowest above-threshold fluence of $F = 1.1 \text{ mJ/cm}^2$, indicate the LA(L)- and LA(X)-zone boundary phonons have been excited at $\nu_{LA}(L) = 3.75 \text{ THz}$ and $\nu_{LA}(X) = 4.34 \text{ THz}$ in this InSb sample. For higher fluence values a red shift in the LA(X)-phonon frequency is observed while the LA(L)-phonon frequency remains unchanged. This downshift in frequency can be attributed to anisotropic charge carrier induced anharmonicity, whereby the large charge carrier density reduces the binding energy for specific crystal bonds so as to preferentially affect LA(X)-phonon propagation and leave the LA(L)-mode unaffected. These observations indicate that anharmonicity in the behaviour of the InSb lattice, and possibly complete

lattice instability, can be induced at excitation fluences significantly less than the damage threshold in InSb.

6.4 References

- [1] M. D. Cummings and A. Y. Elezzabi, “Ultrafast impulsive excitation of coherent longitudinal acoustic phonon oscillations in highly photoexcited InSb,” *Appl. Phys. Lett.* **79**, 770 (2001).
- [2] Value listed on the Certificate of Analysis (checked by: Walerian Kipiniak) for the InSb sample purchased from El-Cat Inc.
- [3] M. S. Bresler, “Chapter 6: Indium Arsenide-Antimonide ($\text{InAs}_{1-x}\text{Sb}_x$),” in *Handbook Series on Semiconductor Parameters*, edited by M. Levinshtein, S. Rumyantsev, and M. Shur, World Scientific Publishing Co. Pte. Ltd., Singapore (1999).
- [4] D. E. Aspen and A. A. Studna, “Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs and InSb from 1.5 to 6.0 eV,” *Phys. Rev. B* **27**, 985 (1983).
- [5] A. M. Lindenberg, I. Kang, S. L. Johnson, T. Missalla, P. A. Heimann, Z. Chang, J. Larsson, P.H. Bucksbum, H. C. Kapteyn, H. A. Padmore, R. W. Lee, J. S. Wark, and R. W. Falcone, “Time-Resolved X-ray Diffraction from Coherent Phonons during a Laser-Induced Phase Transition,” *Phys. Rev. Lett.* **84**, 111 (2000).
- [6] D. L. Price, J. M. Rowe, and R. M. Nicklow, “Lattice Dynamics of Grey Tin and Indium Antimonide,” *Phys. Rev. B* **3**, 1268 (1971).
- [7] Ping Gu, Masahiko Tani, Kiyomi Sakai, and T.-R. Yang “Detection of terahertz radiation from longitudinal optical phonon-plasmon coupling modes in InSb film using an ultrabroadband photoconductive antenna,” *Appl. Phys. Lett.* **77**, 1798 (2000).

- [8] T. K. Cheng, J. Vidal, H. J. Zeiger, G. Dresselhaus, M. S. Dresselhaus, and E. P. Ippen, "Mechanism for displacive excitation of coherent phonons in Sb, Bi, Te, and Ti_2O_3 ," *Appl. Phys. Lett.* **59**, 1923 (1991).
- [9] H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus, "Theory for displacive excitation of coherent phonons," *Phys. Rev. B* **45**, 768 (1992).
- [10] S. Hunsche, K. Wienecke, T. Dekorsy, and H. Kurz, "Impulsive Softening of Coherent Phonons in Tellurium," *Phys. Rev. Lett.* **75**, 1815 (1995).
- [11] A.V. Kuznetsov and C. J. Stanton, "Chapter 7: Theory of Coherent Phonon Oscillations in Bulk GaAs," in *Ultrafast Phenomena in Semiconductors*, edited by Kong-Thon Tsen, Springer-Verlag, New York (2001).
- [12] P. Stampfli and K. H. Bennemann, "Theory for the instability of the diamond structure of Si, Ge, and C induced by a dense electron-hole plasma," *Phys. Rev. B* **42**, 7163 (1990); "Dynamical theory of the laser-induced lattice instability of silicon," *Phys. Rev. B* **46**, 10 686 (1992); "Time dependence of the laser-induced femtosecond lattice instability of Si and GaAs: Role of longitudinal optical distortions," *Phys. Rev. B* **49**, 7299 (1994).

Chapter 7

Conclusion

Through the use of a time-resolved pump-probe reflectivity experimental system capable of resolving material dynamics which occur on femtosecond timescales, this thesis has explored the nature of three distinct semiconductor systems: the initial femtosecond inter-carrier interactions in bulk SI-GaAs, the sub-100 fs field screening by photo-excited carriers in an edge-illuminated GaAs PC switch and lattice mode softening in InSb. This displays both the versatility and the high inherent time-resolution of the experimental technique.

In particular, the temporal evolution of $N = 2.6 \times 10^{18} \text{ cm}^{-3}$ to $N = 2.8 \times 10^{19} \text{ cm}^{-3}$ charge carriers in SI-GaAs within the first 200 fs of photo-excitation was observed, with 25 fs resolution. Based on the third order polarization response, an empirical model was developed in order to determine the fundamental time constants governing the shape of the reflectivity curves. Through a least squares fitting routine, the time constant characterizing the initial reflectivity peak, τ_I , was extracted. The density dependence of τ_I suggests it characterizes the momentum dephasing which occurs from like-mass carrier-carrier scattering, although the numerical values, between 6 and 20 fs, and the functional form are slightly different than measured by other techniques [1,2]. The magnitude of the second time constant was suggestive of a mechanism such as electron-heavy-hole and/or carrier-phonon scattering occurring on a slightly longer timescale than the momentum dephasing time.

The above study indicates it is possible to extract fundamental constants governing the ultrafast temporal dynamics of semiconductor systems through the modelling of time-resolved reflectivity measurements. Two improvements to the current model would improve the accuracy of the time constants extracted. The dissimilar duration of the pump and probe pulses is likely a source of error and could be corrected by the inclusion of separate pump and probe temporal pulse widths in any future model. This would no doubt improve upon the results, but a more detailed phenomenological description of the semiconductor physics which shape the reflectivity curve would lead to a clearer interpretation of the data. While the most effective method of modelling the changes in absorption, hence, reflectivity is through the time evolution of the carrier distribution functions of a photo-excited semiconductor, this is a daunting task. As a result, a simpler model, such as utilised by A. J. Sabbah [3], may enable extraction of accurate numerical values without the added complexity of Monte Carlo simulations.

The dynamics resulting from the photo-generation of $5.6 \times 10^{18} \text{ cm}^{-3}$ carriers into the high-field region of an edge-illuminated PC switch was studied time-resolved reflectivity measurements via bias voltage-lock-in detection. It was determined that the initial decrease in the reflectivity signal within 100 fs of photo-excitation represented a screening of the applied field by the charge carriers and indicates a strong electric field, $|\mathbf{E}_T| \approx 45 \text{ kV/cm}$, is present near the anode of the PC switch. In addition, the ultrafast screening of the bias field within 100 fs of photo-excitation indicates that an electrical transient on the order of 110 fs may be generated through edge-illumination of the PC

switch and provides support for the field screening model of ultrashort electrical pulse generation put forth by Sano and Shibata [4].

Oscillations in the reflectivity signal, at $\nu_2 = 8.0$ THz, and $\nu_3 = 8.8$ THz, were identified as the screened and bare LO-phonon frequencies, respectively, resulting from coupled plasmon-phonon oscillations within different density regimes of the probe spot. In addition, a frequency component at $\nu_I = 7.4$ THz was interpreted as the plasmon-phonon coupled mode which resulted after side-valley scattering removed all but $N = 1 \times 10^{18} \text{ cm}^{-3}$ carriers from the central conduction band valley approximately within 70 fs of photo-excitation. The conclusion drawn from the above information is coupled carrier-lattice dynamics are important in the sub-picosecond electric field screening which occurs in an edge-illuminated PC switch.

This study demonstrates that the lattice plays a role in the screening dynamics of PC switches. However, a more complete examination of the lattice participation in the time evolution of the field within the PC gap may yield valuable information on the basic physics governing the field dynamics. In particular, detailed measurements for various gap sizes, applied fields and probing regions within the gap should be undertaken. In addition, observation of the field dynamics within PC switches deposited on other materials such as InSb may yield interesting results.

In another experiment, transient pump-probe reflectivity measurement of InSb subject to a very large photo-generated charge carrier density ($N > 10^{20} \text{ cm}^{-3}$) resulted in the first time domain observation of coherent LA-phonon modes in this material. These modes, centred at $\nu_{LA}(L) = 3.75$ THz and $\nu_{LA}(X) = 4.34$ THz, were apparent only for excitation

above a threshold fluence of 1.0 mJ/cm^2 and were shown to originate as a result of a displacive excitation process. A dramatic red-shift in the frequency of the LA(X)-phonon mode was observed for fluences beyond 1.1 mJ/cm^2 , while the LA(L)-mode frequency remained unaltered over the same fluence range. This behaviour was attributed to an anisotropic charge carrier induced anharmonicity, and indicates that the lattice may progress towards an unstable regime at fluences well below the damage threshold of InSb.

An unfortunate limitation to the degree of mode softening observed was the maximum output power of the Ti:Sapphire oscillator utilised in this experiment. Through the use of higher focusing power optics, such as a reflective objective, the peak energy fluence could be increased by a factor of more than two. Another alternative is to use the output from the amplifying stage of the Ti:Sapphire laser system, which would allow study of the phonon mode dynamics from the observed threshold energy fluence to beyond the irreversible damage threshold. While the temporal resolution and excitation duration would be increased to 30-40 fs this should not greatly affect the measured signal, as the oscillation period of the phonon modes exceed 200 fs. A more fundamental problem is the lower repetition rate of the amplifier over the Ti:Sapphire oscillator. Through careful management of the excitation conditions, detection electronics and by increasing data integration times this experimental design could be utilised to extend our knowledge of anharmonic oscillations and lattice instability in InSb and other III-V semiconductors.

References

- [1] P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, "Femtosecond Photon Echoes from Band-to-Band Transitions in GaAs," *Phys. Rev. Lett.* **61**, 1647 (1988).
- [2] M. T. Portella, J.-Y. Bigot, R. W. Schoenlein, J.E. Cunningham, and C. V. Shank, "*k*-space carrier dynamics in GaAs," *Appl. Phys. Lett.* **60**, 2123 (1992).
- [3] A. J. Sabbah and D. M. Riffe, "Femtosecond pump-probe reflectivity study of silicon carrier dynamics," *Phys. Rev. B* **66**, 165 217 (2002).
- [4] E. Sano and T. Shibata, "Mechanism for subpicosecond electrical pulse generation by asymmetric excitation," *Appl. Phys. Lett.* **55**, 2748 (1989).

Appendix A

Least Squares Fitting Code

Below is the code utilised in the fitting of the GaAs time-resolve reflectivity curves discussed in Chapter 4. All numeric integrations were accomplished via Simpson's 1/3 rule and the resultant theoretical curves fit to the data via a standard least squares algorithm. The code is written using MicroSoft Visual C++ 6.0.0.

```
#include "stdafx.h"
#include "new_matrix.h"
#include <fstream.h>
#include <iostream.h>
#include <math.h>
#include <string>
using namespace std;

// Data set information (For loading and saving)
const int SetNumber = 1;           // Data set to be loaded
const int Points     = 1000;      // Number of points in the loaded data set

// Invariant parameters.
const int N   = 500;              // Number of points to fit
double  dt    = 0.463;            // Temporal resolution of the data (fs)
double  tmax  = (N-1)*dt;         // Maximum time for the data set (fs)

double  tp    = 10.0              // FWHM (fs) of the optical pump & probe pulses
double  ts    = tp/1.76274717;    // Sech(t/ts)
double  to    = 100.0;            // Pump-probe overlap time

// Initial values for the data fit.
double  percentage = 0.1;         // Percent change of variables (between consecutive
                                   // iterations) which ends the fitting
double  A   = 1.0;               // Ratio of  $2C_{xxyy}/2C_{xyyx}$ ,  $1C_{xxyy}/1C_{xyyx}$ 
double  c1  = 1.0;               // Weight of part 1 of the response =  $4*1c_{ijkl}*t_s*t_s$ 
double  c2  = 1.0;               // Weight of part 1 of the response =  $4*2c_{ijkl}*t_s*t_s$ 
double  t1  = 10.0;              // First relaxation time
double  t2  = 50.0;              // Second relaxation time
```



```

double to2 = 20.0;           // Second relaxation onset time

double Eta;                  // Value of eta at one time
double delta;                // Commonly used function

double OuterIntegral(int, double, double, double, int, int); // Outer integration
double InnerIntegral(int, double, double, int);              // Inner Integration
double OuterFunction(int, double);                           // Outer integration function
double InnerFunction(int, double);                           // Inner integration function
double InnerLimit(int, double);                              // Sets the limit for the inner integration

int main(int argc, char* argv[])
{
    double ExptResp[N];    // Experimental data array
    double tau[N];         // Time array
    double eta[N];         // Commonly used function

    double B1[N];          // 1st term of Beta response
    double B2a[N];         // 2nd term of Beta (a = 1, b = -exp[(t-t`)/t2] term)
    double B2b[N];         // 2nd term of Beta (a = 1, b = -exp[(t-t`)/t2] term)
    double G1[N];          // 1st term of Gamma response
    double G2a[N];         // 2nd term of Gamma (a = 1, b = -exp[(t-to2-t`)/t2] term)
    double G2b[N];         // 2nd term of Gamma (a = 1, b = -exp[(t-to2-t`)/t2] term)
    double TheoResponse[N]; // Sum of above six terms
    double Diff[N];         // Difference between the exp't and theo. data

    double dTRdc1[N]; // Derivative of TheoResponse wrt c1
    double dTRdc2[N]; // Derivative of TheoResponse wrt c2
    double dBdt1[N];  // Derivative of Beta wrt t1
    double dBdt2[N];  // Derivative of Beta wrt t2
    double dGdt1[N];  // Derivative of Gamma wrt t1
    double dGdt2[N];  // Derivative of Gamma wrt t2
    double dTRdt1[N]; // Derivative of TheoResponse wrt t1 (dBdt1 +dGdt1)
    double dTRdt2[N]; // Derivative of TheoResponse wrt t2 (dBdt2 +dGdt2)
    double dTRdto2[N]; // Derivative of TheoResponse wrt to2 (dBdto2 +dGdto2)
    double dTRdA[N];  // Derivative of TheoResponse wrt A

    // Arrays used in the least squares fitting routines
    double z[6][N];
    double zT_z[6][6];
    double Inverse[6][6];
    double zT_z_Inverse_zT[6][N];
    double identity[6][6];

    // Decide whether to do a full fit or a single iteration trial
    double answer1 = 3;

```



```

while ((answer1 != 1) & (answer1 != 9)) {
    cout<<"Full Fit (Press 9) or Single Iteration (Press 1)?"<<endl;
    cin>>answer1;
    cout<<endl;
    if (answer1 == 1) {
        cout<<"SINGLE ITERATION in progress"<<endl;
    }
    if (answer1 == 9) {
        cout<<"FULL FIT in progress"<<endl;
    }
}

// Opens the file to be analysed and puts it into an array
::ifstream ExptResponse;
ExptResponse.open("FILENAME HERE.txt", ios::nocreate);

if(ExptResponse.is_open()){
    cout<<"File opened successfully"<<endl;
    cout<<endl;
}
else{
    cout<<"File did not open"<<endl;
    abort();
    return 0;
}
for (int i = 0; i<= N-1 ; i++) {
    ExptResponse>>ExptResp[i];
//    cout<<"ExptResp["<<i<<"] = "<<ExptResp[i]<<endl;
}

// Opens the file to which the data fit and fit info will be saved
// Defines the output files.
::ofstream DataFitArray, DataFitInfo;
::ofstream Beta1Array, Beta2aArray, Beta2bArray;
::ofstream Gamma1Array, Gamma2aArray, Gamma2bArray;
::ofstream dBdt1Array, dBdt2Array, dGdt1Array, dGdt2Array;

// Opens the output files.
DataFitArray.open("FILENAME HERE.txt");
Beta1Array.open("FILENAME HERE.txt");
Beta2aArray.open("FILENAME HERE.txt");
Beta2bArray.open("FILENAME HERE.txt");
Gamma1Array.open("FILENAME HERE.txt");
Gamma2aArray.open("FILENAME HERE.txt");
Gamma2bArray.open("FILENAME HERE.txt");
dBdt1Array.open("FILENAME HERE.txt");

```



```

dBdt2Array.open("FILENAME HERE.txt");
dGdt1Array.open("FILENAME HERE.txt");
dGdt2Array.open("FILENAME HERE.txt");
DataFitInfo.open("FILENAME HERE.txt");

```

// Print initial parameters

```

DataFitInfo<<"File Info for:
FitOfFeb18(2002)Set"<<SetNumber<<"_"<<N<<"PTS.txt"<<endl;
DataFitInfo<<"Data Set Fitted:
Feb18(2002)Set"<<SetNumber<<"_"<<Points<<"PTS.txt"<<endl;
DataFitInfo<<endl;
DataFitInfo<<"Number of points fitted = "<<N<<endl;
DataFitInfo<<"Precision of the fit = "<<percentage<<" %"<<endl;
DataFitInfo<<endl;
DataFitInfo<<"INITIAL PARAMETERS"<<endl;
DataFitInfo<<"tp = "<<tp<<" fs"<<endl;
DataFitInfo<<"to = "<<to<<" fs"<<endl;
DataFitInfo<<"A = "<<A<<endl;
DataFitInfo<<"c1 = "<<c1<<endl;
DataFitInfo<<"c2 = "<<c2<<endl;
DataFitInfo<<"t1 = "<<t1<<" fs"<<endl;
DataFitInfo<<"t2 = "<<t2<<" fs"<<endl;
DataFitInfo<<"to2 = "<<to2<<" fs"<<endl;
DataFitInfo<<endl;

```

// Initialises the least squares fitting array

```

double delR[6]; // Difference array for the least squares fitting
delR[0] = 1.0e3; delR[1] = 1.0e3; delR[2] = 1.0e3;
delR[3] = 1.0e3; delR[4] = 1.0e3; delR[5] = 1.0e3;

```

// Initialises the time and eta arrays

```

double kappa = 0.0; // Value used to keep integrals from diverging
for(int i1 = 0; i1 <= N-1; i1++){
    tau[i1] = kappa + i1*dt;
    eta[i1] = exp(-2*(i1*dt-to)/ts);
}
delta = exp(2*to2/ts);

```

int w = 0; // Integer to keep track of the number of iterations for the loop.

// LEAST SQUARES FITTING LOOP

```

while( (abs(delR[0]/c1*100.0) >= percentage) || (abs(delR[1]/c2*100.0) >=
percentage) || (abs(delR[2]/t1*100.0) >= percentage) || (abs(delR[3]/t2*100.0) >=
percentage) || (abs(delR[4]/to2*100.0) >= percentage) || (abs(delR[5]/A*100.0) >=
percentage)) {
    w++;
}

```


// Initialises arrays which involve += operations

```
for(int ii1 = 0; ii1 <= 5; ii1++) {
    for(int ii2 = 0; ii2 <= 5; ii2++) {
        zT_z[ii1][ii2] = 0.0;
        identity[ii1][ii2] = 0.0;
        Inverse[ii1][ii2] = 0.0;
    }
    for(int ii3 = 0; ii3 <= N-1; ii3++) {
        zT_z_Inverse_zT[ii1][ii3] = 0.0;
    }
    delR[ii1] = 0.0;
}
```

// Defines each element of Eta to pass to the integrand

```
for (int j1 = 0; j1 <= N-1; j1++) {
    Eta = eta[j1];
}
```

// Generates the Theoretical response curve

```
B1[j1] = c1*eta[j1]*OuterIntegral(3, 0.0001, 0.001, 0.999, 250, 250);
B2a[j1] = c2*eta[j1]/(1-eta[j1])*OuterIntegral(1, 0.0, 0.000001, 0.999999, 2, 100000);
B2b[j1] = -c2*exp((to2)/t2)*eta[j1]*OuterIntegral(2, 0.0001, 0.001, 0.999, 250, 250);
```

```
G1[j1] = c1*exp(-(tau[j1]-to)/t1)*OuterIntegral(5, 0.00001, 0.0001, 0.9999, 250, 250);
```

```
G2a[j1] = c2/((eta[j1]*delta-1)*(eta[j1]*delta-1))*(eta[j1]*delta*(log(eta[j1]*delta)-1)+1);
```

```
G2b[j1] = -c2*exp(-(tau[j1]-to)/t2)*OuterIntegral(4, 0.00001, 0.001, 0.999, 250, 250);
```

```
TheoResponse[j1] = B1[j1] + B2a[j1] + B2b[j1] + A*(G1[j1] + G2a[j1] + G2b[j1]);
```

// Generates the derivatives for the least squares fitting

```
dBdt1[j1] = c1*ts/(2*t1*t1)*eta[j1]*(OuterIntegral(8, 0.0001, 0.001, 0.999, 350, 350) - OuterIntegral(9, 0.0001, 0.001, 0.999, 350, 350));
```

```
dBdt2[j1] = -B2b[j1]*to2/(t2*t2) - c2*ts/(2*t2*t2)*eta[j1]*exp(to2/t2)*(OuterIntegral(6, 0.0001, 0.001, 0.999, 350, 350) - OuterIntegral(7, 0.0001, 0.001, 0.999, 350, 350));
```

```
dGdt1[j1] = (tau[j1]-to)*G1[j1]/(t1*t1) + c1*ts/(2*t1*t1)*exp(-(tau[j1]-to)/t1)*(OuterIntegral(12, 0.00001, 0.0001, 0.9999, 250, 250) - OuterIntegral(13, 0.00001, 0.0001, 0.9999, 250, 250));
```



```
dGdt2[j1] = (tau[j1]-to-to2)*G2b[j1]/(t2*t2) - c2*ts/(2*t2*t2)*exp(-(tau[j1]-to-
to2)/t2)*(OuterIntegral(10, 0.0001, 0.001, 0.999, 250, 250) - OuterIntegral(11, 0.0001,
0.001, 0.999, 250, 250));
```

```
dTRdc1[j1] = (B1[j1] + A*G1[j1])/c1;
dTRdc2[j1] = (B2a[j1] + B2b[j1] + A*(G2a[j1] + G2b[j1]))/c2;
dTRdt1[j1] = dBdt1[j1] + A*dGdt1[j1];
dTRdt2[j1] = dBdt2[j1] + A*dGdt2[j1];
dTRdto2[j1] = (B2b[j1] + A*G2b[j1])/t2;
dTRdA[j1] = G1[j1] + G2a[j1] + G2b[j1];
```

```
// Generates the difference of the Theo. and Exp't response for the least squares fitting
```

```
Diff[j1] = ExptResp[j1] - TheoResponse[j1];
```

```
z[0][j1] = dTRdc1[j1];
```

```
z[1][j1] = dTRdc2[j1];
```

```
z[2][j1] = dTRdt1[j1];
```

```
z[3][j1] = dTRdt2[j1];
```

```
z[4][j1] = dTRdto2[j1];
```

```
z[5][j1] = dTRdA[j1];
```

```
if (answer1 == 1) {
```

```
    cout<<(double(j1+1)/N)*100<<" %"<<endl;
```

```
}
```

```
}
```

```
// VARYING THE PARAMETERS FOR THE LEAST SQUARES FITTING
```

```
// First stage of matrix manipulation: (zT*z)
```

```
for(int j2 = 0; j2 <= 5; j2++) {
```

```
    for(int j3 = 0; j3 <= j2-1; j3++) {
```

```
        for(int j4 = 0; j4 <= N-1; j4++) {
```

```
            zT_z[j3][j2] += z[j2][j4]*z[j3][j4];
```

```
        }
```

```
        zT_z[j2][j3] = zT_z[j3][j2];
```

```
    }
```

```
    for(int j5 = 0; j5 <= N-1; j5++) {
```

```
        zT_z[j2][j2] += z[j2][j5]*z[j2][j5];
```

```
    }
```

```
}
```

```
// Call matrix inversion routine and relabels the inverse
```

```
matrix the_inverse(6,6);
```

```
for(int k1 = 0; k1 <= 5; k1++) {
```

```
    for(int k2 = 0; k2 <= 5; k2++) {
```

```
        the_inverse.setvalue(k1,k2,zT_z[k1][k2]);
```

```
    }
```

```
}
```

```
the_inverse.invert();
```



```

for(int k3 = 0; k3 <= 5; k3++) {
    for(int k4 = 0; k4 <= 5; k4++) {
        Inverse[k3][k4]=the_inverse.getvalue(k3,k4);
    }
}

// Multiplies the inverse by zT
for(int j6 = 0; j6 <= N-1; j6++) {
    for(int j7 = 0; j7 <= 5; j7++) {
        for(int j8 = 0; j8 <= 5; j8++) {
            zT_z_Inverse_zT[j7][j6] += Inverse[j7][j8]*z[j8][j6];
        }
    }
}

// Final multiplication (zT*z)^(-1)*zT*D = delR
for(int j9 = 0; j9 <= 5; j9++) {
    for(int j10 = 0; j10 <= N-1; j10++) {
        delR[j9] += zT_z_Inverse_zT[j9][j10]*Diff[j10];
    }
}

```

// New parameter values

```

c1  = c1  + delR[0];
c2  = c2  + delR[1];
t1  = t1  + delR[2];
t2  = t2  + delR[3];
to2 = to2 + delR[4];
A   = A   + delR[5];

```

// Displays the parameters after each iteration

```

cout<<"Iteration "<<w<<endl;
cout<<"c1  = "<<c1<<" , % change = "<<(delR[0])/c1*100.0<<endl;
cout<<"c2  = "<<c2<<" , % change = "<<(delR[1])/c2*100.0<<endl;
cout<<"t1  = "<<t1<<" fs"<<" , % change = "<<(delR[2])/t1*100.0<<endl;
cout<<"t2  = "<<t2<<" fs"<<" , % change = "<<(delR[3])/t2*100.0<<endl;
cout<<"to2 = "<<to2<<" fs"<<" , % change = "<<(delR[4])/to2*100.0<<endl;
cout<<"A   = "<<A<<" "<<" , % change = "<<(delR[5])/A*100.0<<endl;
cout<<endl;

```

```

if (answer1 == 1) {
    for (int l=0; l<=N-1 ; l++) {
        DataFitArray<<TheoResponse[l]<<endl;
        Beta1Array<<B1[l]<<endl;
        Beta2aArray<<B2a[l]<<endl;
        Beta2bArray<<B2b[l]<<endl;
    }
}

```



```

        Gamma1Array<<G1[l]<<endl;
        Gamma2aArray<<G2a[l]<<endl;
        Gamma2bArray<<G2b[l]<<endl;
        dBdt1Array<<dBdt1[l]<<endl;
        dBdt2Array<<dBdt2[l]<<endl;
        dGdt1Array<<dGdt1[l]<<endl;
        dGdt2Array<<dGdt2[l]<<endl;
    }
    DataFitArray.close();
    Beta1Array.close();
    Beta2aArray.close();
    Beta2bArray.close();
    Gamma1Array.close();
    Gamma2aArray.close();
    Gamma2bArray.close();
    dBdt1Array.close();
    dBdt2Array.close();
    dGdt1Array.close();
    dGdt2Array.close();

    // Abort loop (for testing purposes)
    if(w == 1){
        abort();
    }
}
}

```

// File output information

// Outputs the DataFit values and fitting info separate files.

```

for (int l=0; l<=N-1 ; l++) {
    DataFitArray<<TheoResponse[l]<<endl;
    Beta1Array<<B1[l]<<endl;
    Beta2aArray<<B2a[l]<<endl;
    Beta2bArray<<B2b[l]<<endl;
    Gamma1Array<<G1[l]<<endl;
    Gamma2aArray<<G2a[l]<<endl;
    Gamma2bArray<<G2b[l]<<endl;
    dBdt1Array<<dBdt1[l]<<endl;
    dBdt2Array<<dBdt2[l]<<endl;
    dGdt1Array<<dGdt1[l]<<endl;
    dGdt2Array<<dGdt2[l]<<endl;
}
DataFitInfo<<"FINAL PARAMETERS"<<endl;
DataFitInfo<<"A  = "<<A<<endl;
DataFitInfo<<"c1 = "<<c1<<endl;
DataFitInfo<<"c2 = "<<c2<<endl;

```



```

DataFitInfo<<"t1 = "<<t1<<" fs"<<endl;
DataFitInfo<<"t2 = "<<t2<<" fs"<<endl;
DataFitInfo<<"to2 = "<<to2<<" fs"<<endl;

// Close the files after writing is complete.
DataFitInfo.close();
DataFitArray.close();
Beta1Array.close();
Beta2aArray.close();
Beta2bArray.close();
Gamma1Array.close();
Gamma2aArray.close();
Gamma2bArray.close();
dBdt1Array.close();
dBdt2Array.close();
dGdt1Array.close();
dGdt2Array.close();

return 0;
}
// Performs a double integration of a function. The upper limit of the inner integration
// may be a function.
// Outer integration routine.
double OuterIntegral(int tag, double au, double av, double bv, int L, int M){
    double deltav = (bv-av)/L;
    double sumv = 0;
    sumv += OuterFunction(tag, av)*InnerIntegral(tag, au,InnerLimit(tag, av),M);

    for(int i=1; i<L/2; i++) {
        sumv += 4.0*OuterFunction(tag, av+deltav*(2.0*i-
1.0))*InnerIntegral(tag, au,InnerLimit(tag, av+deltav*(2.0*i-1.0)),M);

        sumv += 2.0*OuterFunction(tag, av+2.0*deltav*i)*InnerIntegral(tag,
au,InnerLimit(tag, av+2.0*deltav*i),M);
    }

    sumv += OuterFunction(tag, bv)*InnerIntegral(tag, au,InnerLimit(tag,
bv),M)+4*OuterFunction(tag, bv-deltav)*InnerIntegral(tag, au,InnerLimit(tag, bv-
deltav),M);

    sumv *= deltav/3.0;

    return sumv;
}
// Inner integration routine.

```



```

double InnerIntegral(int tag, double au, double bu, int M){
    double deltau = (bu-au)/M;
    double sumu = 0;

    sumu += InnerFunction(tag, au);
    for(int i=1; i<M/2; i++) {
        sumu += 4.0*InnerFunction(tag, au+deltau*(2.0*i-1.0));
        sumu += 2.0*InnerFunction(tag, au+2.0*deltau*i);
    }
    sumu += InnerFunction(tag, bu)+4*InnerFunction(tag, bu-deltau);
    sumu *= deltau/3.0;

    return sumu;
}

```

// Outer integral function.

```

double OuterFunction(int tag, double v){
    if(tag == 1){
        return 1.0;
    }
    if(tag == 2){
        return pow((1/v-1),ts/(2*t2))/(Eta+v*(1-Eta));
    }
    if(tag == 3){
        return pow((1/v-1),ts/(2*t1))/(Eta+v*(1-Eta));
    }
    if(tag == 4){
        return pow((1/v-1),ts/(2*t2));
    }
    if(tag == 5){
        return pow((1/v-1),ts/(2*t1));
    }
    if(tag == 6){
        return pow((1/v-1),ts/(2*t2))/(Eta+v*(1-Eta));
    }
    if(tag == 7){
        return pow((1/v-1),ts/(2*t2))/(Eta+v*(1-Eta))*log(1/v-1);
    }
    if(tag == 8){
        return pow((1/v-1),ts/(2*t1))/(Eta+v*(1-Eta));
    }
    if(tag == 9){
        return pow((1/v-1),ts/(2*t1))/(Eta+v*(1-Eta))*log(1/v-1);
    }
    if(tag == 10){
        return pow((1/v-1),ts/(2*t2));
    }
}

```



```

    }
    if(tag == 11){
        return pow((1/v-1),ts/(2*t2))*log(1/v-1);
    }
    if(tag == 12){
        return pow((1/v-1),ts/(2*t1));
    }
    if(tag == 13){
        return pow((1/v-1),ts/(2*t1))*log(1/v-1);
    }

    return 0.0;
}

```

// Inner integral function.

```

double InnerFunction(int tag, double u){
    if(tag == 1){
        return log((u*(1-Eta*delta)+Eta*delta)/(Eta*u*(1-
delta)+Eta*delta))/(u*(1-Eta)+Eta);
    }
    if(tag == 2){
        return pow((1/u-1),-ts/(2*t2))/(Eta+u*(1-Eta));
    }
    if(tag == 3){
        return pow((1/u-1),-ts/(2*t1))/(Eta+u*(1-Eta));
    }
    if(tag == 4){
        return pow((1/u-1),-ts/(2*t2));
    }
    if(tag == 5){
        return pow((1/u-1),-ts/(2*t1));
    }
    if(tag == 6){
        return pow((1/u-1),-ts/(2*t2))/(Eta+u*(1-Eta))*log(1/u-1);
    }
    if(tag == 7){
        return pow((1/u-1),-ts/(2*t2))/(Eta+u*(1-Eta));
    }
    if(tag == 8){
        return pow((1/u-1),-ts/(2*t1))/(Eta+u*(1-Eta))*log(1/u-1);
    }
    if(tag == 9){
        return pow((1/u-1),-ts/(2*t1))/(Eta+u*(1-Eta));
    }
    if(tag == 10){
        return pow((1/u-1),-ts/(2*t2))*log(1/u-1);
    }
}

```



```

    }
    if(tag == 11){
        return pow((1/u-1),-ts/(2*t2));
    }
    if(tag == 12){
        return pow((1/u-1),-ts/(2*t1))*log(1/u-1);
    }
    if(tag == 13){
        return pow((1/u-1),-ts/(2*t1));
    }

    return 0.0;
}

// Inner integral upper limit.
double InnerLimit(int tag, double v){
    if(tag == 1){
        return 1.0;
    }
    if(tag == 2){
        return v/(v*(1-delta)+delta);
    }
    if(tag == 3){
        return v;
    }
    if(tag == 4){
        if(v/(v*(1-Eta*delta)+Eta*delta) >= 0.99999) {
            return 0.99999;
        }
        else {
            return v/(v*(1-Eta*delta)+Eta*delta);
        }
    }
    if(tag == 5){
        if(v/(v*(1-Eta)+Eta) >= 0.99999) {
            return 0.99999;
        }
        else {
            return v/(v*(1-Eta)+Eta);
        }
    }
    if(tag == 6){
        return v/(v*(1-delta)+delta);
    }
    if(tag == 7){
        return v/(v*(1-delta)+delta);
    }

```



```

    }
    if(tag == 8){
        return v;
    }
    if(tag == 9){
        return v;
    }
    if(tag == 10){
        if(v/(v*(1-Eta*delta)+Eta*delta) >= 0.999999) {
            return 0.999999;
        }
        else {
            return v/(v*(1-Eta*delta)+Eta*delta);
        }
    }
    if(tag == 11){
        if(v/(v*(1-Eta*delta)+Eta*delta) >= 0.999999) {
            return 0.999999;
        }
        else {
            return v/(v*(1-Eta*delta)+Eta*delta);
        }
    }
    if(tag == 12){
        if(v/(v*(1-Eta)+Eta) >= 0.999999) {
            return 0.999999;
        }
        else {
            return v/(v*(1-Eta)+Eta);
        }
    }
    if(tag == 13){
        if(v/(v*(1-Eta)+Eta) >= 0.999999) {
            return 0.999999;
        }
        else {
            return v/(v*(1-Eta)+Eta);
        }
    }
    return 0.0;
}

```


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